ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

THE EFFECTS OF PARTIALLY ACRYLATED HYPERBRANCHED POLYESTERS ON UV CURABLE COATINGS

M.Sc. THESIS

Saadet Şeyma ÖZDEMİR

Department of Chemistry

Chemistry Programme

MAY 2014

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

THE EFFECTS OF PARTIALLY ACRYLATED HYPERBRANCHED POLYESTERS ON UV CURABLE COATINGS

M.Sc. THESIS

Saadet Şeyma ÖZDEMİR
(509111027)

Department of Chemistry

Chemistry Programme

Thesis Advisor: Prof. Dr. H. Ayşen ÖNEN

MAY 2014

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KISMİ AKRİLLENMİŞ ÇOK DALLI POLİESTERLERİN UV İLE KÜRLENEBİLEN KAPLAMALARDAKİ ETKİSİ

YÜKSEK LİSANS TEZİ

Saadet Şeyma ÖZDEMİR
(509111027)

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Prof. Dr. H. Ayşen ÖNEN

MAYIS 2014

Saadet Şeyma ÖZDEMİR, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 509111027, successfully defended the **thesis** entitled **THE EFFECTS OF PARTIALLY ACRYLATED HYPERBRANCHED POLYESTERS ON UV CURABLE COATINGS**", which he/she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. H. Ayşen ÖNEN** Istanbul Technical University	.....
Jury Members :	**Prof. Dr. Nilgün Kızılcan** Istanbul Technical University	.....
	Prof. Dr. Fatoş Yüksel Güvenilir Istanbul Technical University	.....

Date of Submission : 05 May 2014
Date of Defense : 29 May 2014

To my parents,

FOREWORD

This study has been carried out in POLMAG Laboratory (Polymeric Materials Research Group), Faculty of Science and Letters, Istanbul Technical University.

First of all, I would like to express my sincere gratitude to my advisor Prof. Dr. H. Ayşen ÖNEN for her guidance and encouragement.

I would like to thank Prof. Dr. İ. Ersin Serhatlı for his technical support.

I also would like to thank Res. Ass. Dr. Tuba ÇAKIR ÇANAK and Ömer Faruk VURUR, Müfide KARAHASANOĞLU, Sümeyye ŞABANİ for their all support, assistance and patient during this study.

I would like to thank Assoc. Prof. Dr. M. Vezir KAHRAMAN, Res. Ass. Emrah ÇAKMAKÇI for their technical support.

Furthermore, I would like to thank very much my friends Fatma CÖMERT, Neşe KAYNAK and Faruk BÜYÜKYORAN for their support and patient.

Finally, I would like to express my profound gratitude to my family, Fehime ÖZDEMİR, Deniz ÖZDEMİR and Buğrahan ÖZDEMİR never avoids their unique support and endless positive energy that I need from me all of my life.

May 2014

Saadet Şeyma ÖZDEMİR
(Chemist)

TABLE OF CONTENTS

Page

ABBREVIATIONS

EtOH	**:** Ethanol
EW	**:** Equivalent Weight
FT-IR	**:** Fourier Transform Infrared Spectrophotometer
MW	**:** Molecular Weight
OH	**:** Hydroxyl group
TGA	**:** Thermal Gravimetric Analysis
UV	**:** Ultra Violet
VOC	**:** Volatile Organic Compound
DB	: Degree of branching
HBP	: Hyperbranched polymers (HBPs)
DPGDA	**:** Dipropyleneglycoldiacrylate
MW	**:** Molecular Weight
NMR	**:** Nuclear Magnetic Resonance Spectroscopy
SCVP	**:** Self Condensing Vinyl Polymerization
TGA	**:** Thermogravimetrical Or Thermo-Gravimetrical Analysis
PAB	**:** Partially acrylated Boltorn H20
PAB100	**:** 100% acrylated Boltorn H20
PAB75	**:** 75% Partially acrylated Boltorn H20
PAB50	**:** 50% Partially acrylated Boltorn H20
PAB25	**:** 25% Partially acrylated Boltorn H20
PAB100-5	**:** 5% weight of formulation is 100% acrylated Boltorn H20
PAB75-5	**:** 5% weight of formulation is 75% partially acrylated Boltorn H20
PAB75-10	**:** 10% weight of formulation is 75% partially acrylated Boltorn H20
PAB75-15	**:** 15% weight of formulation is 75% partially acrylated Boltorn H20
PAB75-20	**:** 20% weight of formulation is 75% partially acrylated Boltorn H20

LIST OF TABLES

Page

LIST OF FIGURES

Page

THE EFFECTS OF PARTIALLY ACRYLATED HYPERBRANCHED POLYESTERS ON UV CURABLE COATINGS

SUMMARY

In the past two decades, the field of dendritic polymers (dendrimers, hyperbranched and higly branched polymers) has been well established with a large variety of synthetic approaches, fundamental studies on structure and properties of these unique materials, and possible applications.

(HBPs) are by now an established class of polymeric materials and can be considered as highly functional specialty products. It is verified that they offer the chance for the development of new products but at the same time they present a challenge due to their complex branched structure. Because of their compact molecular shape, presence of large number of end groups and lack of chain entanglement are quite different from their conventional linear counter-parts. And also (HBPs) are inexpensive to produce and easy to synthesize in large quantities. By modification of the end groups the properties of (HBPs), e.g. glass transition temperature, solubility and miscibility, melt viscosity, as well as surface properties, are significantly determined and define mainly possible applications. Dendrimers are monodisperse molecules with well-defined, perfectly branched architectures, made in a multi-step organic synthesis. In contrast, hyperbranched polymers (HBPs) are made in a one-pot polymerization, making them promising candidates for industrial applications where ultimate perfection in structural uniformity is less needed. (HBPs) are highly branched macromolecules with a three-dimensional dendritic architecture, less regular in structure and their degree of branching (DB) typically does not exceed 50% of that of dendrimers.

Hydroxyl functional aliphatic polyesters based on 2,2-di(methylol)propionic acid (DMPA) are one of the most widely investigated families of hyperbranched polymers. Synthesis of hyperbranched polmyers from DMPA with various core molecules such as glycerol, trimethylol propane or pentaerithtritol were reported in the literature.

Epoxy acrylates which include epoxy groups are find widely used area in coating industry. Because the aromatic epoxy acrylates provide high hardness, reactivity and chemical resistance, as well as hyperbranched resins. Because of the presence very reactive double bonds, acrylated resins go acrylate polymers easily.

Photopolymerization is one of the most rapidly expanding processes for materials production. Applications of photopolymerization are being further developed and provide a number of economic advantages over the usual thermal operations: solvent-free formulations, low energy input, room temperature treatment and Iow costs, and also helping the environment to reduce significantly volatile organic compounds.

During the past decade, photopolymerization has been practically applied in variety of areas, including printing inks, adhesives, surface coating, printing plates and microelectronics. The main applications of UV is described, starting with the classical ones on temperature sensitive substrates, like wood, paper and plastics, where the UV-curable coatings are already well established.

Photocrosslinkable polymers found a widespread application areas. UV curing method is applied to crosslink rapidly photosensitive polymers in order to obtain thick cross-sections instead of heating.

Hyperbranched polyesters end-capped with various groups capable of undergoing photopolymerization in UV curing applications. It was reported that hyperbranched polyesters provide a unique combination of coating properties such as high hardness, scratch resistance and flexibility, whereas at the same time ensuring low viscosity and low shrinkage.

In this study, hydroxyl functional hyperbranched aliphatic polyester, Boltorn H20, was partially acrylated with acrylic acid and characterization were performed by FT-IR and ^{1}H NMR spectroscopic techniques. UV curable formulations were modified by gradual replacement of epoxy acrylate oligomer with partially acrylated Boltorn H20. The effects of partially acrylated Boltorn H20 against the epoxy acrylate in the coating formulations were evaluated. Mechanical, thermal, physical properties of UV-cured films were investigated.

KISMİ AKRİLLENMİŞ ÇOK DALLI POLİESTERLERİN FOTOPOLİMERİZASYON İLE KÜRLENEBİLEN KAPLAMALARDAKİ ETKİSİ

ÖZET

Son yirmi yılda, benzersiz fiziksel-kimyasal ve yapısal özellikleri sayesinde dendiritk polimerler (dallanmış, çok dallanmış ve hiperdallanmış polimerler) alanında yapılan çok çeşitli çalışmalar ve sentetik yaklaşımlar tez konusu olmuş, önem kazanmıştır. Dallanmış (dendritic) polimerler 3 boyutlu yapıda olup, başlıca dallanmış (dendrimer) ve çok dallanmış (hyperbranched) polimerler olarak sınıflandırılabilir.

Çok dallanmış polimerler, yüksek sayıda reaktif son grup içermeleri sayesinde çok fonksiyonel özellikli ürünler olup artık polimerik malzeme sınıflandırılmalarında ayrıca yer almaktadır. Kompleks dallanmış yapısal özellikleri sayesinde yeni ürün geliştirilmesinde meydan okuyan imkanlar sağlamaktadır. Çok sayıda reaktif son grup içermeleri, düşük viskozite, iyi çözünürlük özellikleri ve zincir yapılarının karmaşıklığı bu polimer sınıfını geleneksel düz zincirli polimerleden farklı tutar. Ayrıca fazla miktarda sentezlenmeye müsait ve üretim maliyeti düşük malzemelerdir. Sentezlenme metodlarının kolay uygulanabilir ve hızlı olması da üretim maliyetindeki düşüklüğün en önemli sebeplerindedir.

Çok dallanmış polimerlerin son gruplarının modifikasyonu ile camsı geçiş sıcaklığı, çözünürlük, karıştırılabilirlik, erime viskozitesi ve yüzey özellikleri gibi bir çok polimerik özellik kontrol edilebilir ve bu durum çok dallanmış polimerlere endüstriyel alanda geniş uygulama imkanları tanır. Dendrimerler iyi tanımlanmış, mükemmel dallanmış mimariye sahip, çok aşamalı organik sentez ile elde edilen moleküllerdir. Dendrimerlerin aksine, çok dallanmış polimerlerin sentezinin kolay, düşük maliyetli ve yüksek verimli olması, onları yapısal homojenlinkte nihai mükemmeliğin daha az gerekli olduğu endüstriyel uygulamalarda yükselen bir aday haline getirmiştir. Çok dallanmış polimerler yüksek derecede dallandırılmış üç boyutlu dentirik mimariye sahip makro moleküllerdir, yapıları dendrimerlerden daha az düzenlidir ve dendrimerler gibi düzenli simetrik yapıya sahip değillerdir.

2,2-di(methylol)propionic acid (DMPA) tabanlı hidroksil fonksiyonel alifatik polyesterler hiperdallanmış polimerin en çok araştırılmış ailesidir. Gliserol, trimetilol propan veya pentaeritritol gibi öz moleküller ile birlikte DMPA kullanılarak gerçekleştirilen hiperdallanmış polimer sentezi literatürde belirtilmiştir olup bu alan için önemli bir örnek teşkil etmektedir.

Epoksi gruplar içeren epoksi akrilatlar, genellikle Diglisidil Eter Bisfenol A ile Akrilik Asidin tepkimesi sonucu ortaya çıkan malzemelerdir ve sahip oldukları düşük viskozite ile hızlı kürlenme özellikleri sayesinde özellikle kaplama endüstirisinde çokça kullanım alanı bulunmaktadır. Çok dallanmış polimerler gibi aromatik epoksi akrilatların da yüksek sertlik, reaktivite ve kimyasal dayanım özelliklerinde sağladığı

iyileştirme, endüstride aldıkları yerin başlıca sebeplerindendir. Çift bağların reaktivitesinin yüksek olmasından ötürü, akrilatlı reçineler akrilik polimerlere kolayca ihtiva ederler.

Işıkla polimerizasyon (fotopolimerizasyon) yöntemi molekülün büyümesi için gerekli gücün ışık enerjisi ile elde edilmesi temeline dayanır. Fotopolimer reçinenin temel yapıtaşı monomerdir. Işığa maruz kaldıklarında oluşan kimyasal reaksiyonla bu monomerler birleşerek polimer moleküllerini oluştururlar. Sıvı haldeki bir fotopolimer reçine polimerizasyon sonrasında çok uzun ve ağır moleküllere sahip olarak katı hale geçer.

Fotopolimerizasyon yöntemi, malzeme üretiminde en hızlı büyüyen alanlardan biridir. Geçmiş yıllarda yaygın olarak kullanılmakta olan ısı kaynaklı polimerik işlemlere kıyasla başta ekonomik olmak üzere, çözücü içermeme, düşük enerji ihtiyacı, oda sıcaklığında uygulanabilirlik, ısıya duyarlı yüzeylerde uygulanabilirlik, hızlı kürlenme, düşük maliyet ve geniş formülasyon aralığı gibi avantajlarının bulunması, ışıkla polimerizasyon işleminin uygulama alanlarının gittikçe gelişmekte olmasına gösterilebilecek başlıca sebeplerdendir. Ayrıca organik bileşenlerin uçmasını önemli derece düşürerek çevreye sağladığı katkı da endüstride tercih sebebi olması için bir diğer önemli gerekçedir. Radyosyanla kürlenebilen kaplamalarda herhangi bir solvent buharlaşması olmaksızın kürlenme prosesini gerçekleşmesinin yanısıra kürlenme daha düşük enerji tüketimi ile gerçekleşir.

Fotopolimerizasyon yöntemi son on yılda, kartuşlar, yapıştırıcılar, yüzey kaplama, boya kaplamaları ve mikroelektronikler gibi çeşitli alanlarda pratikte uygulanmaktadır. En önemli uygulama alanı ahşap, kağıt ve plastik gibi ısıya duyarlı yüzeyler olarak belirlenmiştir. Bu nedenle endüstriye pararlel olarak bu çalışmada, ahşap yüzey kaplamalarında kullanılması amaçlanan akrillenmiş polyester poliollerin davranışları ve mekanik özellikleri incelenmektedir.

Bununla beraber, ışıkla çapraz bağlanabilen polimerler de fotopolimerizasyonun uygulama alanında geniş ölçekte yer sahibi olmuştur. Fotopolimerizasyon yöntemi bu alanda ısıya hassasiyet gösteren yüzeylerde hızlı kürleşmeyi sağlayan yani hızlı çapraz bağ oluşumunu sağlayan başlıca metottur.

Çok dallanmış polimerler içerdikleri yüksek sayıdaki çeşitli fonksiyonel-son gruplarla fotopolimerizasyon uygulamaları için çok uygun sağlayıcılardır. Bu polimerlerin yüksek sertlik, çizilme dayanımı ve esneklik gibi benzersiz kaplama özellikleri sunarken aynı zamanda düşük viskosite ve düşük esneme sağladığı yapılan araştırmalar ve deneyler sonucunda belirlenmiştir. Çok dallanmış polimerlerin belirtilen avantajlara sahip olmasının en büyük sebebi fonksiyonel grupların sayısının yüksek olmasıdır ve ayrıca bu fonksiyonel grupların elde edilmek istenen özellik doğrultusunda kontrol edilebilir olması da bir diğer tercih sebebidir. Benzer şekilde çok dallanmış polyester poliol olan Boltorn H20 16 adet OH fonksiyonel gruba sahiptir ve bu çalışmada fonksiyonel grupların akrillenmesi gerçekleşmiştir.

Bu çalışmada hidroksil özellikli hiperdallanmış alifatik polyster olan Boltorn H20, akrilik asit ile 25%, 50%, 75% ve 100% oranlarında kademeli olarak artırılarak kısmi akrillenmiştir. FT-IR spektroskopisi tekniği ile akrillenme reaksiyonunun gerçekleşmesi kontrol edilmiş ve H^1 NMR spektroskopik tekniği ile de karakterizasyon yapılarak deneysel sonuçlara göre akrillenme yüzdeleri elde

edilmiştir. Teorik veriler ve deneysel hesaplamalar kıyaslanarak verim/ akrillenme yüzdesi hesaplanmıştır.

Epoksi akrilatlarla benzer özelliklere sahip olması sebebiyle film formulasyonları hazırlanırken epoksi akrilat yerine kısmi akrillenmiş Boltorn H20 kullanılarak reçinenin kürlendikten sonraki mekanik özellikleri ve davranışlarının incelenmesi çalışmanın temel amacıdır. Bu nedenle UV kürleme formulasyonları, epoksi akrilat oligomeri yerine kısmı akrillenmiş Boltorn H20' nin kademeli olarak ilavesi sonucu modifiye edilmiştir. Boltorn H20' nin akrillenme yüzdesindeki artışın kürlenmiş filmin özelliklerine etkisinin belirlenmesinin yanısıra sabit akrillenme yüzdesindeki Boltorn H20'den miktarca artırılarak hazırlanan formulasyonların kürlenmiş filme etkisi de bir diğer araştırma konusu olmuştur.

Formulasyonda, fotopolimerizasyon tepkimesinin UV ışığı altında gerçekleşmesini sağlayan başlatıcı, filme esneklik sağlayan üretan akrilat, dayanıklılık sağlayan epoksi akrilat ve yine dayanıklılık sağlayan akrillenmiş Boltorn H20 kullanılmıştır. Epoksi akrilat ve akrillenmiş Boltorn H20' nin formulasyonlardaki toplam miktarı sabit tutulmuş olup, akrillenmiş Boltorn H20 yüzdece artırılırken epoksi akrilat aynı oranda azaltılmıştır. Kaplama formulasyonları kürlendikten sonra kısmı akrilatlı Boltorn H20'nin epoksi akrilata göre etkileri yorumlanmıştır. UV-kürleme işlemine tabi olan formulasyonlarda mekanik, termal, fiziksel ve yüzey özellikler incelenmiştir.

1. INTRODUCTION

Before the early 1980s all dendritic architectures and networks were known only as naturally occurying structures/entities found either in the abiotic world (eg. snow crystals, lightning patterns, erosion / river network fractals) or in the biological realm. Certain randomly branched, dendritic architectures were hypothesized by Nobel Laureate P. Flory as early as the 1940s to describe theoretical polymer intermediates in crosslinking events. However, it was not until the late 1970s that the first examples of such dendritic architectures were intentionally synthesized and rigorously characterized in a laboratory. The widely recognized terms were first coined and introduced by Tomalia in 1983 to describe compositionally broad and diverse categories of precisely defined core-shell, dendritic structure [1].

Dendritic means highly branched tree-like structures and covers both, dendrimers as well as hyperbranched polymers but also other highly branched or fractal molecules; dendrimers are perfectly branched molecules prepared in a step-wise manner with the potential to come close to structural and molar mass uniformity; on the other hand hyperbranched polymers are not fully branched, and have less regular structure than that of dendrimers, and they can be synthesized by simple one-pot polymerizations on a larger scale [2].

HBPs polymers allow to design very well the polymer properties by the structural units and by the end groups. No or low crystallinity, low solution viscosity, and better solubility, miscibility, and specific melt viscosity behavior in comparison with linear model polymers are general, well-acknowledged features of HBPs polymers. These properties dominate the high potential for applications in, for example, coating and resin applications and as additives for linear polymers. Moreover, their use in high-tech applications, such as catalysis, microelectronics, thin film technology, and sensorics, is increasing strongly [3].

Epoxy resins have more than one epoxy groups that can be converted into the thermoset forms and they have repeat units effects the end-use applications of the resin like hyperbranched polymers. Epoxy resins provide thin-layer durable coatings having

mechanical strength and good adhesion to a variety of substrates since epoxy resins play important role in coating industry as chemical and special purpose coatings [4]. Epoxy acrylates prepared by catalysed reaction of an epoxy groups with either acrylic or methacrylic acid, respectively [5].

Acrylates contain vinyl groups, that is, two carbon atoms double bonded to each other directly attached to the carbonyl carbon. And also they easily go polymer forms because the double bonds are very reactive and they are common monomers in polymer plastics, forming the acrylate polymers.

UV-curing is one type of coatings has been established as an alternative curing mechanism to thermal curing for sensitive substrates like wood, paper and plastics. UV-radiation curing has become a well accepted thecnology which has found a large variety of industrial applications because of its distinct advantages. Acrylate-based resins and reactive diluents are preferred in most photocuring applications because of their superior reactivity [6].

In this thesis, the study is aimed to synthesize and characterize partially acrylated hyperbranched polyester and prepared UV curable film formulation modified with partially acrylated polyester and epoxy acrylate. And also to investigate UV-curable film properties according to degree of acrylation and amount of acrylated HBPs instead of epoxy acrylate.

2. THEORETICAL PART

2.1 Hyperbranched Polymers

The chemistry and physics of dendritic compounds started two decade ago. Today, this science of uniquely shaped molecules, namely, dendrite-shaped moleculs, is one of the most exciting topics of contemporary interdisciplinary research. The dendrimers and their related molecules have been investigated widely not only from the viewpoints of synthetic, physical and material chemistries but also from the mathematics. In this decade, all chemistry research fields have adopted and applied the dendrimers and dendrimer methodologies [7]. Dendritic polymer are recognized new architectural class with a young but well established body of interdisciplinary research exploring a remarkable variety of potential applications [8]. Dendritic polymers synthesized from AxB monomers comprise monodisperse dendrimers with exact branching and irregularly branched, polydisperse, hyperbranched polymers. They have a number of very unique and different properties compared to their linear analogs; for instance, at high enough molecular weight they were found toThey are classified due to degree of structural control into three different categories random hyperbranched polymers, dendigraft polymers and dendrimers.

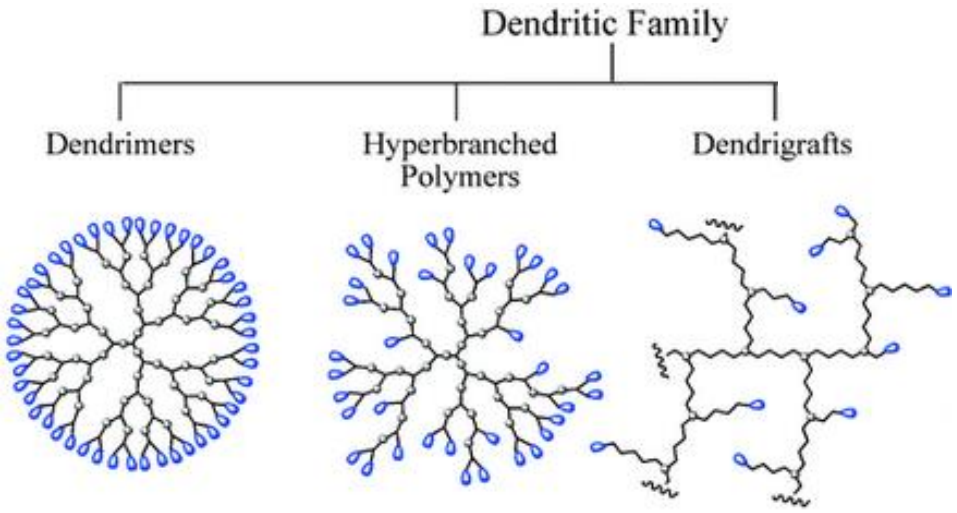


Figure 2.1 : Classification of dendritic macromolecules.

Dendrimers are highly uniform, monodisperse polymers globular structure and large number of functional groups.

Dendigrafts polymers can be regarded as semi-control branched polymer architectures intermediate in terms of structure control between dendrimers and hyperbranched polymers [9].

Hyperbranched macromolecules are another class of dendritic polymers which highly branched, also treelike and globular in nature, but less highly branched and significantly less regular than the dendritic systems.

Owing to their macromolecular structures and their properties, hyperbranched polymers represent a transition between linear polymers and highly branched dendrimers.

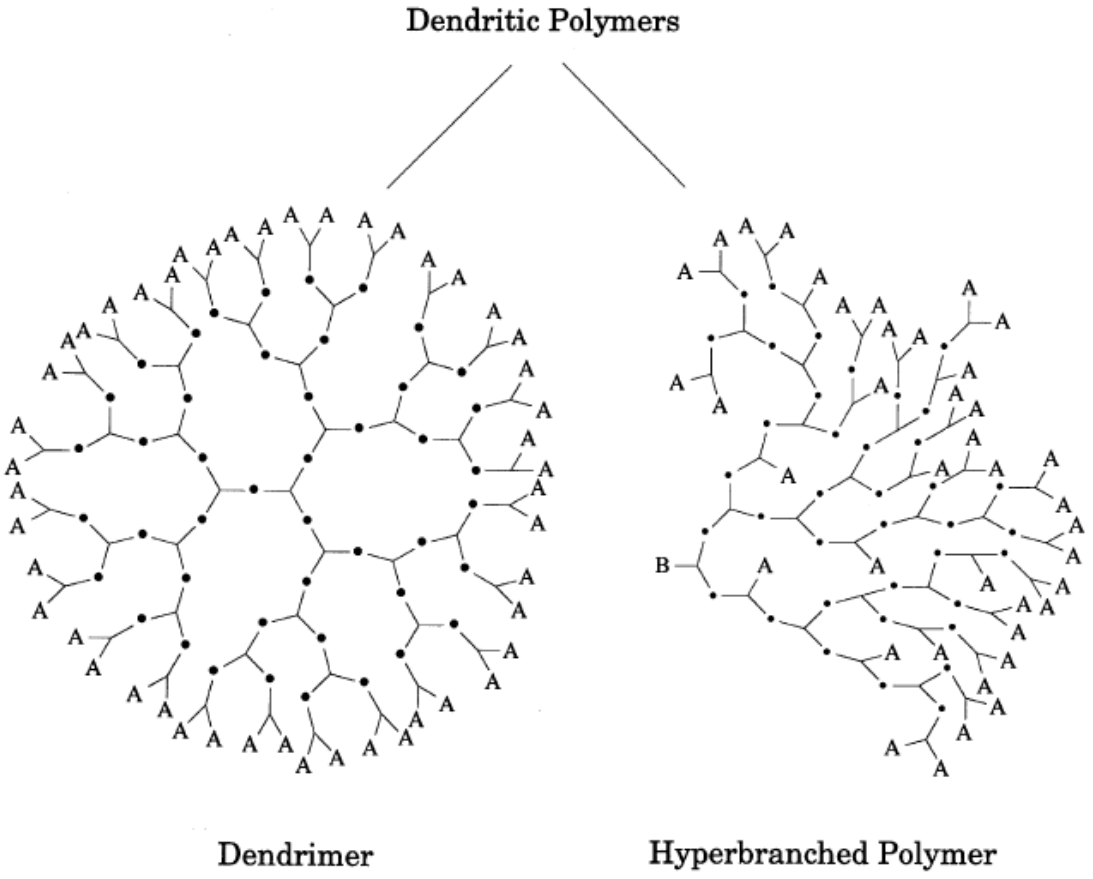


Figure 2.2 : Schematic description of dendritic polymers comprising dendrimers and hyperbranched polymers.

Polymerization of AxB monomers yields highly branched polymers, with a multitude of end groups, which are less prone than linear polymers to form entanglements and undergo crystallization.

Hyperbranched polymers are phenomenologically different from linear polymers; for example, the lack of entanglements results in lower viscosity than in linear polymers of the same molecular weight. They shows high solubility. The thermal properties of hyperbranched polymers have been shown to depend on the nature of the chain ends. The lower the polarity, the lower the glass transition temperature since it is suggested that the glass transition of hyperbranched polymers is due to translational motions.
Owing to their promising applications, extensive efforts have been made to characterize, understand and theoretically describe their structure-property relationship such as the molecular weight and distribution degree of branching (DB) intramolecular cyclization etc.

They are densely branched molecules with a globular structure, leading to lower viscosity and many end-groups, creating property-designing opportunities [10].

In addition, the excellent thermal stability that can be designed into a hyperbranched polymer as well as modulus properties qualify these products as polymer additives. Their chemical and physical structure can solve the problems related to processability, property compromises, and compatibility, which are found with commercial additives and modifiers.

The main drawback with dendrimers and hyperbranched polymers was that they were normally synthesized using a stepwise process which make them far too expensive to be used as polymer additives [11].

Now hyperbranched polymers are generally produced by the one-pot polymerization of AB_X-type monomers or macromonomers involving polycondensation, ring opening or polyaddition reactions. Hence, the products usually have broad, statistical molecular weigth distributions, much as is observed for traditional polymers [12].

Unlike dendrimers, hyperbranched polymers are often easy to synthesize on a large scale and therefore are considered to be alternatives for dendrimers [13].

Hyperbranched compounds, which do not have perfect structures owing to their method of synthesis, show polydisperse properties because they contain molecules of different masses [14].

The final properties of hyperbranched polymers are determined firstly, by the structure of the repeating unit, and secondly, by the nature of the resulting end groups, or even vice-versa [15]. Most of applications of hyperbranched polymers are based on the absence of chain entanglements, the globular shape, and the nature and the large number of functional groups within a molecule. Modification of the number and type of functional groups on hyperbranched polymer is essential to control their solubility, compatibility,reactivity, adhesion to various surfaces, self-assembly, chemical recognition, and electrochemical and luminescence properties properties. the large number of functional groups allow for the tailoring of their thermal, rheological, and solution properties and thus provides a powerfull tool to design hyperbranched polymers for a wide variety of applications [16].

Growing international community of researchers is exploring or developing a variety of uses for dendritic polymers. These include catalysts, micelle mimics, magnetic resonance imaging agents, additives and etc. For some areas, such as coating resins and tougheners in epoxy-resins, hyperbranched polymers are foreseen to play an important role [17].

2.1.1 Synthesis of hyperbranched polymers

The synthesis of hyperbranched polymers can often be simplified compared to that of dendrimers as it does not require the use of protection/deprotection steps. This is due to the fact that hyperbranched polymers are allowed to contain some linearly incorporated AxB monomers. The most common synthesis route follows a one-pot procedure where AxB monomers are condensed in the presence of a catalyst. Another method using a core molecule and an AxB monomer has also been described. The lower cost of synthesizing hyperbranched polymers allows them to be produced on a large scale, giving them an advantage over dendrimers in applications involving large amounts of material, although the properties of hyperbranched polymers are intermediate between those of dendrimers and linear polymers [18].

Synthesis of dendrimers or hyperbranched polymers has become a major research interest due to their highly branched structure with very different characteristic features from linear polymers, such as relatively low viscosity, high solubility, and having a large amount of pending, peripheral or side functional groups.

Preparation of dendrimers requires a high degree of purity of the starting materials and high yields of the individual synthetic steps, all of which generally increases the effort involved. Polydisperse, hyperbranched compounds, which admittedly show defects yet often display properties smiliar to their ideally perfect dendritic relations, can readily be synthesised. Synthesis of hyperbranched polymers proceeds in a single-stage process via;

- Polycondensation
- Self-condensing vinyl polymerization (SCVP)
- Self condensing ring-opening polymerization and proton-transfer polymerization [19].

Hyperbranched polymers are prepared in one-step procedures, most common by polycondensation of AB*x* monomers, as reported by Stockmayer [20].

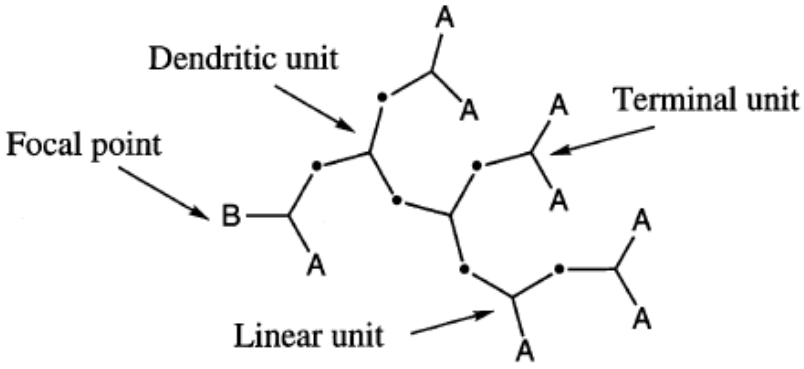


Figure 2.3 : Different segment types present in hyperbranched polymers.

Reaction of the functional F groups with the functional C (coupling) groups of a second monomer molecule gives rise to randomly branched molecules. Since the C groups are present in excess (n≥2) crosslinking reactions are avoided from the outset. Reaction can be brought to a standstill by addition of stopper components. Since the synthesis of hyperbranched polymers does not involve coupling to core molecule but only FCn monomers react with one another, both branched molecules and linear sequences may

be formed. If reactive groups are present during the synthesis of hyperbranched polymers, then a protective group technique is required because the desires molecular architecture would otherwise not be formed [21].

2.1.2 Applications of hyperbranched polymers

Hyperbranched polymers have irregular structure with high polydispersity but the ease of the synthetic procedures and the globular shape together with the high number of functional groups make them effective for industrial applications.

These polymers can be applied as toughеners for thermosets, curing, crosslinking or adhesive agent, compatibilizers, catalysis and etc. Their application area is given on figure 2.4.

Table 2.1 : Applications of hyperbranched polymers.

Applications of Hyperbranched Polymers	
• Paper coatings • Oil field chemicals • Fuel additives • Textile chemicals • Additives and resins for waterborn applications • Oligomer precursos for UV-curing applications • Adhesives • Dispersion agent • Rheology modifier • Elastomer crosslinkers • Foam agent • Wetting agent • Lubricant • Emulsifier • Membranes	• Hydrogel components for tissue-growth active hydrogels • Anchor for catalysts • Magnetic resonance imaging agents • Drug delivery agents • Immunodiagnostics • Globular templates • Dye transfer inhibitor • Catalysis, micelles • Plastics additives • Dental composites • Moisture retention in cosmetics • Controlled release agent • Processing aid • Photosensitive materials • Sensor materials • Toughеners

2.1.3 Properties of hyperbranched polymers

2.1.3.1 Degree of branching

The degree of branching can be regarded as the ratio of branched units in the polymer to those in a perfect dendrimer. Thus the limiting values are DB=0 for linear polymers and DB=1 for a perfect dendrimer [22]. DB is one of the most important parameters of hyperbranched polymers because of the fact that it is directly correlating with the density of the polymer structure and the number and location of the end groups [23].

2.1.3.2 Thermal properties

The glass transition temperature (Tg) is one of the most important thermal parameter for a dendritic polymer. Upon heating, amorphous componenets convertfrom a glassy stateto a liquid state at Tg. Due to complex structure of hyperbranched polymers segmental motions also effected by the branching points and the presence of numerous functional groups. The glass transition temperature of a hyperbranched polymer is not only affected by the chain-end composition, but also by the molar mass and the macromolecular composition [24].

For dendritic polymer systems Tg increases with generation number to a limit, above which it remains nearly constant. The increase in Tg with generation number is assumed to reflect a decrease in chain mobility due to branching. The chemical nature of the large number of terminal groups strongly effects the glass transition temperature [25].

The thermal stability of hyperbranched polymers is related to the chemical structure in the same manner as for linear polymers; for example, aromatic esters are more stable than aliphatic ones. In one case, the addition of a small amount of a hyperbranched polyphenylene to polystyrene was found to improve the thermal stability of the blend as compared to the pure polystyrene [26].

2.1.3.3 Mechanical and rheological properties

The presence of numerous terminal groups is a typical characteristic of hyperbranched polymers. The terminal groups can affect the properties of the polymer and provide versatile scaffolds for further modification. Changes in properties related to the architecture of hyperbranched polymers rather than the chemical structure.

Hyperbranched polymers are often referred to as amorphous polymers since the branching of the backbone reduces the ability to crystallize in the same manner as linear polymers.

One application that has been suggested for hyperbranched polymers is as an additive, where the hyperbranched polymers improve a property such as polymer toughness.

The resulting thermoset polymer exhibited a dramatic increase in toughness while retaining the high modulus of the original thermoset.

Since highly branched globular structure, the configuration of hyperbranched polymers and dendrimers are coined by a lack of chain entanglements. The non-entangled state shows poor mechanical properties, resulting in brittle dendritic polymers with limited use as thermoplastics [27]. The stress-strain behavior of hyperbranched polymers can be similar to that of soft/ductile metals. Like ductile metals, hyperbranched polyesters do not strain harden. This is due to their structure which does not permit the process of chain extension and orientation (the usual mechanism of strain hardening) [28].

2.2 Epoxy Resins

Thermoset epoxy composites are most often used in high-performance applications on account of their unique performance-to-cost ratio compared to polyester-based composites. They generally possess excellent properties and are suitable for a large number of processing techniques. This results from the different chemistries, blending components and pre-polymerisation stages that can be used. Despite their versatility, the applications they are intended for, demand an increasingly high performance. In particular, resin-related properties such as the glasstransition temperature (Tg), toughness, and dimensional stability are of prime interest. In general, as the glass transition temperature of a resin system is raised, a decrease in toughness and dimensional stability is observed. This depends on the fact that these properties are all related to the cross-link density of the cured resins, which rigidifies the molecular

network, decreases its deformability, and increases the process-induced shrinkage [29-31].

This significantly reduced their cost without affecting the basic properties of dendritic-like molecules. As these HBPs show viscosity properties typical of dendritic polymers, they are commercially viable modifiers for engineering materials [32].

Epoxy resins are well-known to exhibit excellent mechanical, thermal and electrical properties, good dimensional stability, and resistance to moisture, corrosion and chemicals. However, the effective usage of cured epoxy resin as structural composites is restricted due to its poor impact resistance which is associated with high brittleness caused by heavily cross-linked structures [33]. This problem has been solved either by reducing the crosslink density of the epoxy network or by toughening the epoxy resin using secondary components such as low molecular weight rubbers functionally terminated engineering thermoplastics rigid phase, and interpenetrating polymer networks [34-38].

However, they can affect the processing ability of epoxy resin by an undesired increase in its viscosity. This problem can be overcome by adding secondary components such as hyperbranched polymers. Hyperbranched polymers possess lower viscosity than linear polymers with the same molar mass, are soluble in most of the organic solvents, their end groups can be tailored, and can be employed as a modifier that can simultaneously act as toughening agents. Boogh and his coworkers employed hyperbranched polymer as a toughener for epoxy resins in 1999 [39]. Hydroxyl-terminated and epoxy-terminated hyperbranched polymers were used to toughen the epoxy resin as a function of varying weight content of the toughening agent [40, 41].

Cured epoxy resins exhibit excellent adhesion to a variety of substrates, good chemical and corrosion resistance, excellent electrical insulation, high tensile, flexural and compressive strength and thermal stability. The largest single use is in coatings, where high chemical and corrosion resistance and adhesion are important.

Properties of Epoxy Resins:

- Chemical resistance
- Easy cure
- Low shrinkage

- High adhesion
- Thermal stability
- Versatility

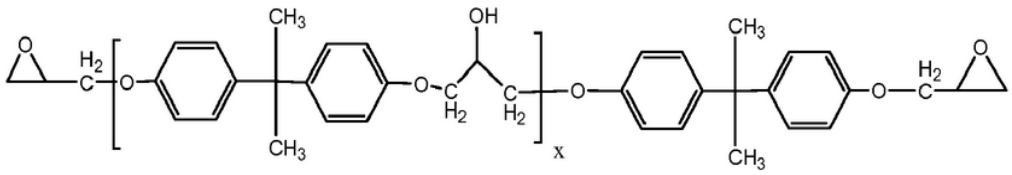


Figure 2.4 : Diglycidyl ether of bisphenol A, DGBA.

The epoxy resins, being thermosets in nature, can not be used alone. They require what is called a hardener to effect the curing of the coating and conversation of the coating into a useful protective.

2.2.1 Epoxy acrylates

Epoxy acrylates are the reaction products of acrylic acid with various diglycidyl ethers of bisphenol A. Epoxy acrylate oligomers are introduce vinyl ester groups with carbon–carbon double bonds at the end of the epoxy resin and they don't have epoxide functionality.

In many industries, epoxy acrylate are generally used, because they have excellent adhesive and non-yellowing properties, flexibility, hardness and chemical resistance. Also, epoxy acrylate oligomers can be used in a wide rage of viscosities and formulations in the form of single- or two-part products [42, 43].

The reaction rate and extent of UV curing were found to be strongly dependent on the concentration of C=C bonds in the epoxy acrylate oligomers. The epoxy backbone imparts toughness to the cured films, while the carbon–carbon and ether bonds ameliorate their chemical resistance. Their reaction with an acid produces hydroxyl groups, thereby introducing polarity, which can improve the wettability of adhesive [44].

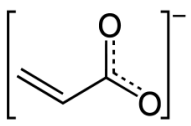


Figure 2.5 : The acrylate anion

However, acrylic compounds have poor thermomechanical stability, because they generally have a linear structure. Therefore, the cross-linking of functional acrylate oligomers and monomers is needed in order to increase their thermomechanical stability. The advantages of functional acrylates include their good adhesion to plastics, high cross-linking density, reactivity, chemical resistance, and hardness and scratch resistance. It is reported that when an adhesive is weakly cross-linked, it shows a fluid-like behavior; however, in the case of a more highly cross-linked adhesive, the creep resistance is greatly increased [45]. Moreover, functional acrylates crosslink quickly by radical and cationic polymerizations [46].

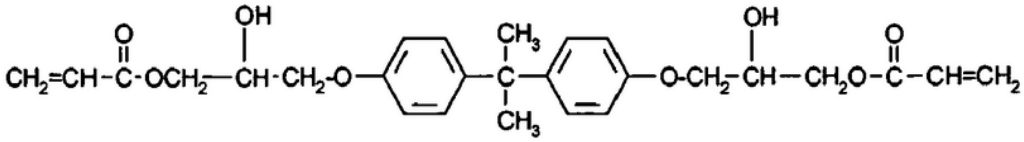


Figure 2.6 : General structure of epoxy acrylate.

The simplest epoxy resin is prepared by the reaction of bisphenol A with epichlorohydrine. The value of repeat units (n) vary from 0 to 25. This determines the end-use applications of the resin.

2.3 Polyesters and Hyperbranched Polyesters

In fibers and plastics, polyester refers to high molecular weight (MW) partially crystalline, linear, thermoplastic polymeric esters of a short-chain diol and terephthalic acid. The first polyesters were developed by Keinle in 1926. After the end of the Second World War, the production of high molecular weight linear polyesters began to be developed on a large scale [47]. Polyesters are made by step-growth polymerization. The relatively low MW polyesters coating are usually made from mixtures of diols, triols and dibasic acids. Most commonly excess polyol is used; hence, the polyesters are hydroxy-terminated polyesters. In coatings, however, it is used to describe a different sort of material. Most coating polyester have relatively low MWs anda re amorphous and branched, and they must be cross-linked to form useful coating films. Furthermore, the term is applied only to certain polyesters, those prepared from polyols and polybasic acids [48].

Polyesters are an important class of condensation polymers, and the availability of a few commercial dihydroxy carboxylic acids has prompted several research groups to

look into hyperbranched polyesters in great detail. Several old patents concerning highly branched and hyperbranched polyesters exist. One of the oldest patents, from 1972, concerns the polymers obtained by condensation of polyhydroxy monocarboxylic acids and their use in coatings. The potential use of hyperbranched polymers as rheology modifiers or for drug delivery purposes was described in patent in 1992. Two of the most recent patents concern hyperbranched polymers obtained from polyols (chain terminator or core molecule) and A2B-monomers and their use in coating applications [49, 50].

The use of aliphatic monomers for hyperbranched polyesters has been debated because aliphatic monomers are said to be prone to thermal degradation reactions such as decarboxylation, cyclization, or dehydration [51]. The only commercial hyperbranched polymer is a hydroxy-functional aliphatic polyester, Boltorn, available from Perstorp AB, Sweden.

2.3.1 Polyester acrylates

Acrylated polyesters are prepared by reacting the OH group of polyesters with acrylic acid or hydroxyl acrylate with acid groups of the polyester structure. Polyester acrylates are often low viscosity resins requiring little or no monomer. They produce coatings and adhesives dominated by the polyester structure used in the oligomer. They are used for strong rigid adhesives.

2.4 Boltorn® H20 Hyperbranched Polyester Polyol

Boltorn® H20 is the highly hyperbranched polyester polyol. It exhibits very good reactivity with low viscosity and enhanced mechanical properties. Boltorn® H20 has 16 terminal hydroxyl groups, with a nominal molecular weight of 1750 g/mole. The product is amorphous with a Tg of 25 °C.

Properties of Boltorn® H20 was supplied from Perstorp AB, Sweden. Boltorn®H20, Boltorn®H30 which has 32 terminal hydroxyl groups and Boltorn®H40 which has 64 terminal hydroxyl groups are given at table 2.1.

Table 2.2 : Properties of Boltorn® H20, H30, H40.

	soluble in	MW, g/mol	mgKOH/g OH	MgKOH/g acid	Tg, C	Viscosity PAS(C)
Boltorn® H20	NMP, Acetone, Glycols	2100	503	4.3	25	6(110)
Boltorn® H30	MeOH, Acetone, NMP	3500	496	4.6	35	40(110)
Boltorn® H40	MeOH, Acetone, MEK	5100	490	6.4	40	80(110)

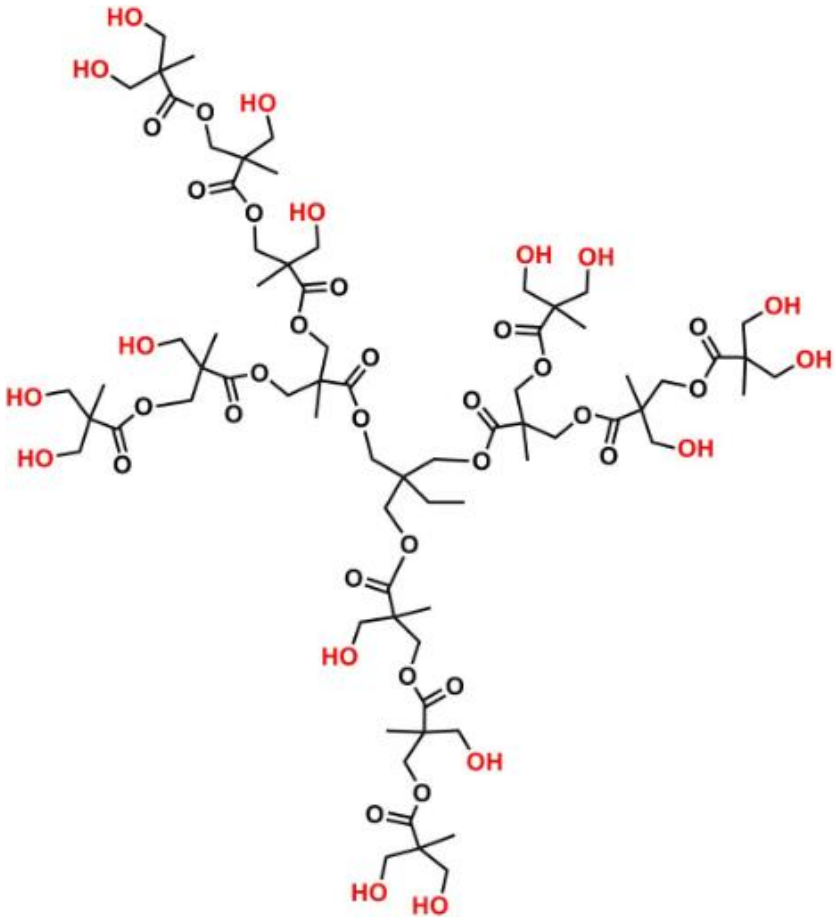


Figure 2.7 : Hyperbranched polyester polyol, Boltorn® H20.

2.5 Photopolymerization

Photopolymerization is a process in which a reactive group undergoes a polymerization process using light-generated radicals and typically involves a liquid solution transforming into a solid upon exposure to light. The liquid solution is a curable formulation of monomers, oligomers, or viscous prepolymers and the solid is a cured material, which is generally a polymer or polymer network. The light may include a wide range of wavelengths depending on the initiator used and the desired application. Most monomers, oligomers, or prepolymers do not produce initiating species with a sufficient quantum yield upon light exposure; therefore, it is necessary to introduce an initiator (low-molecular-weight organic molecule) to start the polymerization.

The history of photopolymerization dates back 4000 years to ancient Egypt, where sunlight was used to cross-link linens for mummification. Today, photopolymerization has become a common technology for a wide variety of applications including coatings, paints, inks, adhesives, photolithography, microfluidics, three-dimensional (3D) prototyping, and biotechnology including dentistry, drug delivery, and regenerative medicine.

Photopolymerization does not require solvents, is economical (low energy consumption), and involves high reaction rates at ambient temperatures, making it attractive for many of these applications. In addition, there is chemical versatility in this technique and spatial and temporal control of the initiation process, which has led to photopolymerization becoming an important processing method. The fast polymerization kinetics at physiological temperature even in the presence of water and oxygen is making photopolymerization a well-recognized method for the fabrication of biomaterials.

The field of polymer photochemistry continues to be recognized as an active area in applied photochemistry, with many topics growing in industrial development. Photopolymerization and photocuring science and technologies are being developed particularly with regard toward designing novel and specific initiators and materials for specialist applications. Interest in active ionic initiators and radical-ionic processes remains a high priority, while the photo-crosslinking of polymers is attractive in terms

of enhancing the physical and mechanical properties of electronic materials and the development of liquid crystalline materials [52].

It is clear that photopolymerizable systems are finding increased utility in many fields, including for biomedical applications. The tunability in properties as well as the controllability of the polymerization process makes this technique desirable and gives rise to diverse materials with a wide range of functionality and processing capabilities. While parameters such as initiation conditions, reaching desirable conversion, toxicity, and final applications must be considered in material design, progress in these areas is being made rapidly. Future research in this area will only improve the properties of these materials and expand the applicability to a wide range of fields.

The photoinitiated radical polymerizations of acrylates and methacrylates comprise the most well-studied and commercially important class of active center photopolymerizations. Contributing significantly to the commercial and academic success of this chemistry has been the development of a wide range of highly sensitive radical photoinitiators.

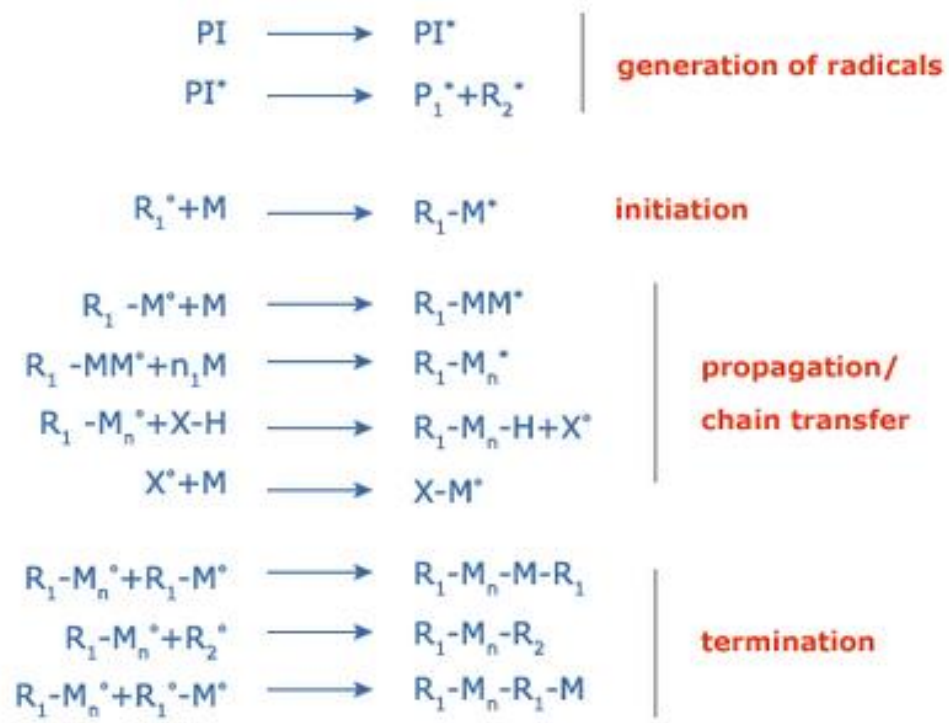


Figure 2.8 : Reaction scheme of radical photopolymerization.

The polymerization causes a change in the coating composition that may result in a significant property alteration, such as change in

• Solubility—printing plates, resists, filters, displays.

• Adhesion—proofing products.

• Phase change—wave guides.

• Change in refractive index—holographic films.

• Change in electrical conductivity—xeroprinting films.

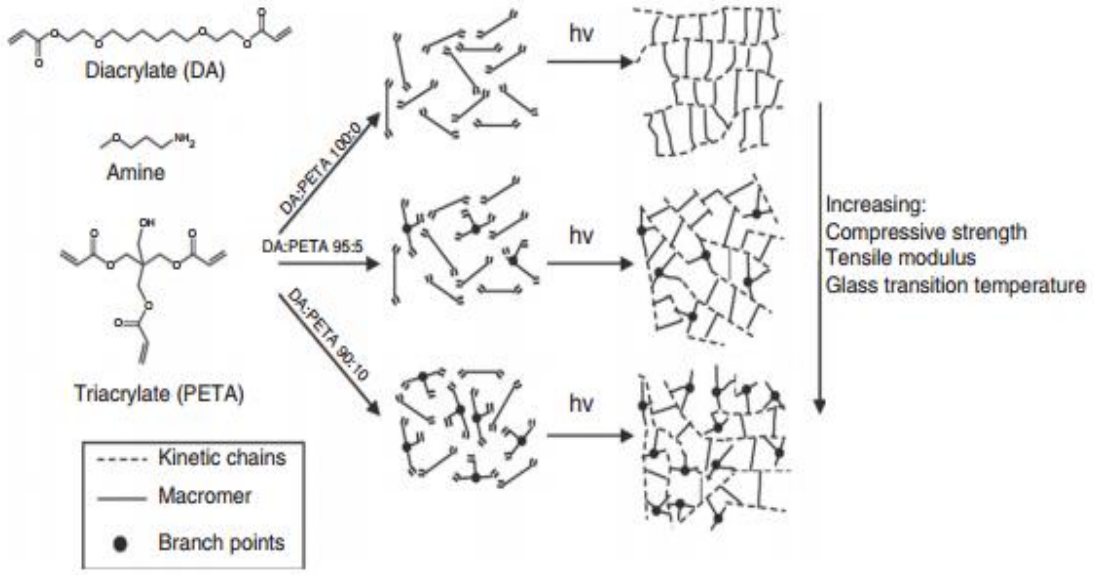


Figure 2.9 : Example of photopolymerization effect on several physical properties of the resulting polymer

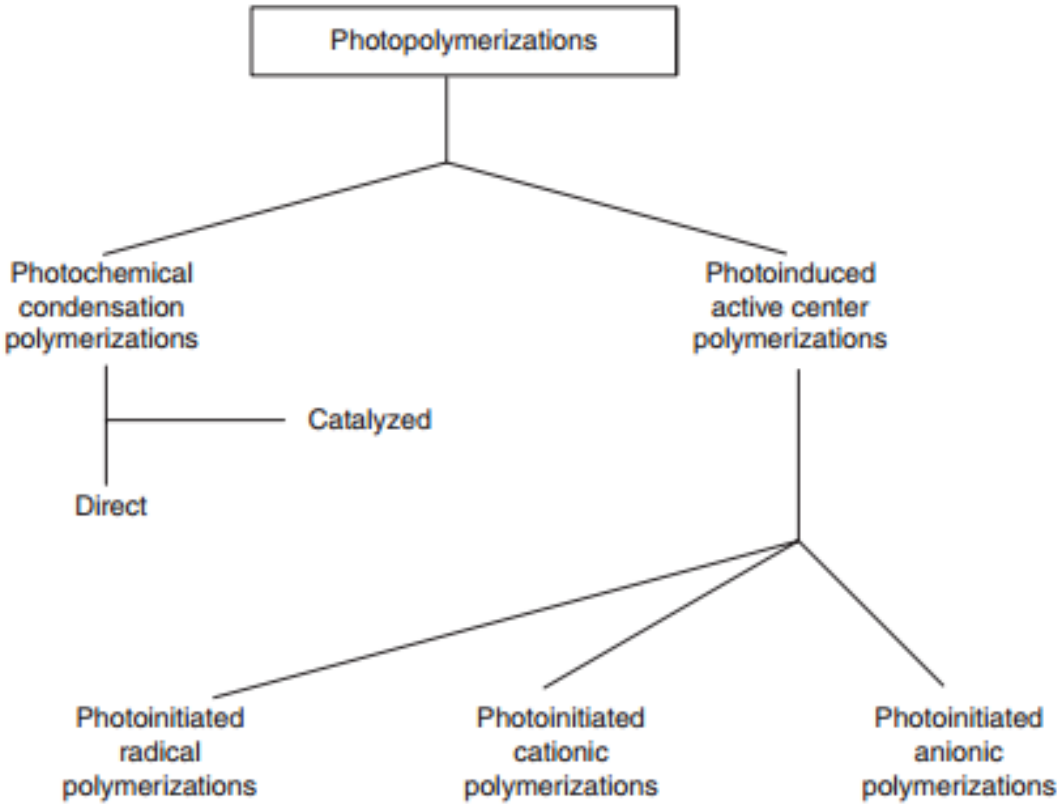


Figure 2.10 : Categories of photopolymerization reactions.

The formulation of the photopolymerizable system will ultimately determine the structural, physical, and mechanical properties of the final product. However, the fast polymerization kinetics and dramatic changes in the material properties during polymerization lead to a complex system with polydisperse polymers and heterogeneities in the cross-link density for networks. In addition, polymer properties are highly dependent on experimental parameters such as light intensity, concentration of the precursors and initiator, and temperature. Therefore, it is important to understand and optimize these parameters for each photopolymerizable system to achieve the desired material properties. For linear polymers, it is possible to manipulate the material characteristics to some extent following postcuring using processes such as annealing and extrusion [53].

2.5.1 Photopolymerization reaction

In a general sense, photoinitiated polymerizations are chain reaction mechanisms that include initiation, propagation, and termination steps during which a liquid solution is commonly converted into a solid polymer or highly cross-linked structure when

multifunctional monomers or macromers are used. During a photopolymerization reaction, initiation is achieved by a photochemical event that occurs when light is absorbed by the initiating molecule. As most monomers, oligomers, or prepolymers do not absorb significant light (mostly transparent) to produce initiating species, a photoinitiator (typically a low-molecular-weight organic molecule) is used to produce reactive initiating species such as radicals or ions. Photopolymerization reactions can be classified into two main categories, namely radical polymerization (e.g., acrylates) and cationic polymerization (e.g., ring-opening reaction of epoxies).

The photoinitiator is specific to the reaction type and its efficiency is determined by its reactivity toward the monomer. The reaction mechanism for a classical photoinitiated radical polymerization is shown in Figure 2.12.

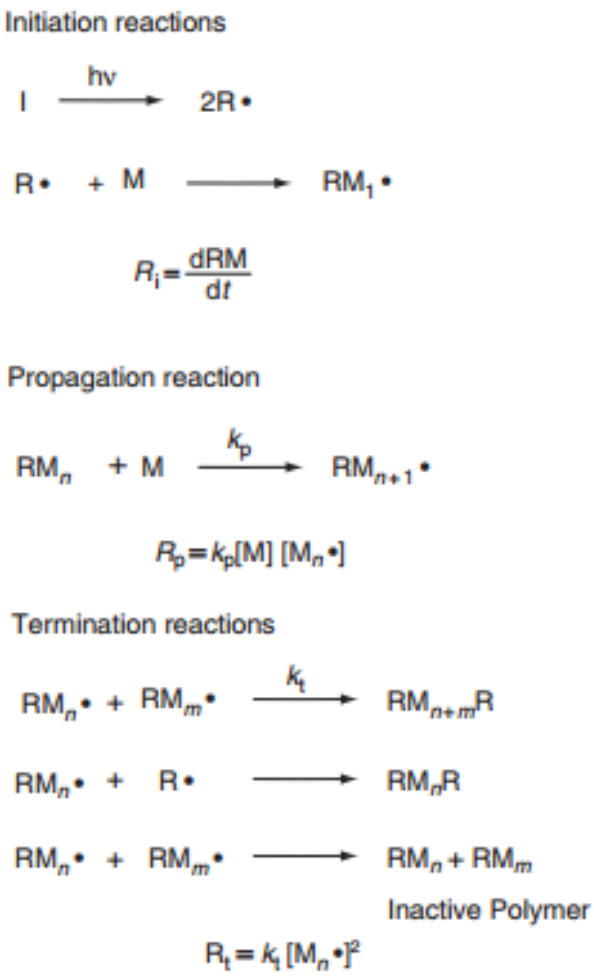


Figure 2.11 : The reaction mechanism for a radical photopolymerization.

The first step is the initiation reaction where the initiator decays into primary radicals with light exposure, which then react with carbon–carbon double bonds on the monomer. The rate of initiation is directly proportional to the light intensity, initiator concentration, molar absorptivity, efficiency and quantum yield of initiation, which denotes the number of initiating species produced per absorbed photon.

The propagation reaction starts when the monomer radical attacks the carbon–carbon double bonds on additional monomers, generating new radicals at the end of the growing chains. Although the propagation reaction is generally considered as chain length independent, there are cases where chain length has a significant effect on the kinetic parameters, depending on the polymer formed and degree of polymerization. The rate of propagation, which is simply the rate of double bond conversion.

In termination, it is important to discuss diffusional limitations with respect to initiation and propagation steps.9 If the termination reaction becomes diffusion controlled, mass transfer of the growing chains becomes even more difficult, leading to an increase in the concentration of radicals. Therefore, the rate of the polymerization significantly increases, which is termed auto acceleration, also referred to as the gel effect.

Termination reactions are also hindered in highly cross-linked systems, where the cross-linking density continuously increases during photopolymerization, which may lead to the trapping of radicals that may remain in the network even for months.

2.5.2 Photoinitiator

One of the most important components of the photopolymerization system is the photoinitiator, which is capable of absorbing light efficiently and generating reactive initiating species. A photoinitiator becomes electronically excited through absorption of light within a given spectral range, and undergoes subsequent reactions to afford reactive species capable of inducing an addition polymerization reaction. Many new photoinitiator systems continue to be developed for photopolymerization. Various types of photoinitiator systems have also been used together with new technological developments in UV.

Photoinitiators are generally specific to the photopolymerization system, and when choosing the photoinitiator, the important properties that should be considered are cost,

odor, shelf life, light absorption, quantum yield of intersystem cross-linking, and reactivity of the initiating species toward monomer when compared with reactivity with oxygen, solvent, and impurities.

The role of a photosensitizer is to absorb the light and transfer the excitation to the initiator molecule, which then reacts with the monomers. The general photoinitiation mechanisms are summarized in Figure 2.12.

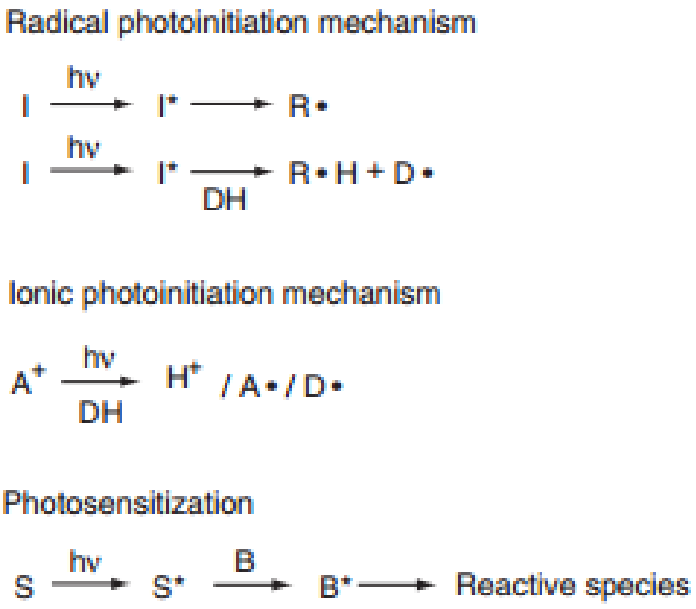


Figure 2.12 : Photoinitiation mechanisms.

While the use of light to break bonds in organic, inorganic, and organometallic compounds to form radicals is a very common process, most of these reactions are inefficient. Two basic types of radical photoinitiators are currently in widespread use due to their high quantum yields of photolysis and because their simple synthesis makes them relatively inexpensive compounds. The first type of radical photoinitiators is unimolecular photoinitiators based on aryl ketones that undergo facile α-cleavage reactions on irradiation with light. The second type of radical photoinitiators is the so-called bimolecular photoinitiators that consist of a diaryl ketone together with a compound that provides easily abstractable hydrogen atoms [54].

1.1.1.1 Unimolecular photoinitiators (type I)

A wide range of α-cleavage photoinitiators have been prepared and are commercially available. Not only have these photoinitiators been optimized to provide high quantum yields for radical production at specific irradiation wavelengths, but they have also

been structurally modified to tailor their solubility and to provide nonyellowing characteristics in the final polymer product.

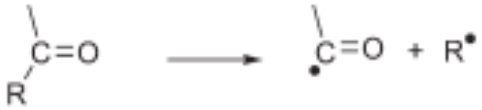


Figure 2.13 : Photo cleavage (α-cleavage, Norrish I, or β-cleavage)

In the search for non-yellowing photoinititators, - α-hydroxyalkylphenones were developed in the eighties: the solid 1-hydroxy-cyclohexyl-phenyl-ketone (HCPK, Figure 2.14) and the liquid 2-hydroxy-2-methyl-1-phenyl-propan-1-one were the first initiators allowing UV curing of clearcoats for commercial applications. In addition a photoinitiator is needed for the UV curable part of the mixture. This initiator is stimulated by UV radiation and produces reactive radicals which initiate the polymerisation of resins with unsaturated double bonds such as polyurethane acrylates, acrylic acrylates, etc [55].

HCPK is used in acrylate formulations and in order to illustrate the high reactivity of HCPK in an acrylate formulation, the conversion of acrylate functions was monitored as a function of the exposure time at room temperature by real-time infrared spectroscopy [56]. Both under air and inert atmosphere, initiation occurs within a fraction of a second while nearly complete conversion of acrylates is achieved within less than 5 seconds. The glass temperature of the final polymer film is too high to allow a complete conversion of the acrylates when UV curing is performed at room temperature, the sample vitrification reducing the chain mobility. However, low amounts of remaining acrylates after curing have little effect on the film properties.

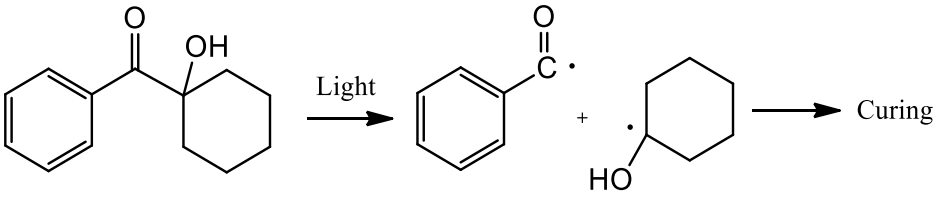


Figure 2.14 : Light induced cleavage of HCPK.

2.5.2.2 Biomolecular photoinitiators (type II)

Some photoinitiator systems require a co-initiator, which does not absorb light but is involved in the production of reactive species.. In some cases, photoinitiation cannot occur directly and requires the presence of other molecules to produce initiating species, such as with a photosensitizer [57].

Figure 2.15 : Intermolecular γ hydrogen abstraction (Norrish II).

The most common of these photoinitiators consists of benzophenone or a substituted benzophenone in combination with an aliphatic tertiary amine. A proposed mechanism for the formation of radicals by these bimolecular photoinitiators. Photoexcitation of benzophenone results in the formation of triplet-state benzophenone that forms a charge transfer complex, with triethanolamine. Formal electron transfer takes place with the subsequent formation of a radical cation–radical anion pair. Proton transfer then occurs with the formation of a carbon-centered radical, 23, and the hydroxy(diphenyl) methyl radical, 24. Radical species 23 initiates polymerization, while 24 primarily undergoes dimerization to form benzopinacol.

1.1.3 Parameters influencing photopolymerization behavior

2.5.3.1 Initiator Properties

The reactivity and the concentration of the photoinitiator molecules are two key factors in photopolymerization reactions. The efficiency of initiating radical generation, quenching by monomers, and bimolecular reactions between initiating radicals and monomers are controlled by the reactiveity of the excited states of the photoinitiator. The yield of initiation or the yield of polymerization (Rp/ I_{abs}, where I_{abs} is the energy absorbed by the initiator) determines the efficiency. Therefore, absorbed overall energy is a controlling factor to determine efficiency, which depends on the extinction coefficient of the electron transition and the position of the absorption band. It is also possible to increase I_{abs} by simply increasing the initiator concentration. Increasing the initiator concentration also increases the number of initiating radicals, which decreases the induction period and can increase the hardness of the cured material. Therefore, the optimum concentration of the initiator has to be determined depending on the

photopolymerizable system used, the experimental conditions, and desired product properties [58].

2.5.3.2 Monomer and oligomer properties in photopolymerization

The nature of the photopolymerizable components such as chemical structure, molecular weight, and functionality plays a significant role in the efficiency of the polymerization reac-tion and physical, chemical, photochemical, mechanical, and structural properties of the cured system. When monomers or multifunctional monomers are combined with oligomers, such as in the case of carbonate, carbamate, or oxazolidone acrylates, they become highly reactive, exhibit low residual saturation and good flexibility [59].

The mechanical properties sharply increase with functionality of the monomer with an increase in the cross-linking density, but they become more brittle. Solubility, biocompatibility, thermal resistance, and photochemical stability are some of the other important parameters that should be considered when choosing the most suitable monomer system.

2.5.3.3 Light source

A wide variety of light sources and wavelengths are available, and are being used in photopolymerization, such as conventional light sources (e.g., mercury lamp), pregelification lamp, low-pressure fluorescent lamp, doped mercury-vapor lamp and microwave-powered lamp, blue light emitting diode (LED), or laser.The spectral distribution, intensity, and temporal dependence of light emission are important parameters characterizing a light source and its use for intended applications.

First, a photoinitiator has to be chosen so that the absorption band of the initiator matches the emission spectrum of the light source. The potential absorption of the light by fillers also needs to be considered. In addition, increasing light intensity, such as in the case of focused beam lasers, shortens the exposure times.

In general, the light source strongly affects the photopolymerization reactions and hence the properties of the cured material.

2.5.3.4 Sample thickness

Sample thickness has two main effects on photopolymerization: light penetration and oxygen inhibition. As the incoming light is absorbed by the initiator molecules, it is

attenuated while it passes through the sample, causing curing problems in thick systems, such as thick coatings and 3D complex structures in orthopedic applications (fillings, pins, and so forth). In photo-cross-linking reactions, this may lead to the formation of highly cross-linked structures at the surface facing the light and lower cross-linking at the bottom, creating a gradient in properties. The rate of polymerization generally increases sharply with sample thickness in photopolymerized coatings, which is not observed when the photopolymerization is carried out under nitrogen. In air, oxygen can easily penetrate into the sample, scavenging the radicals, and the oxygen diffusion rate is also dependent on film thickness.

2.5.3.5 Oxygen

It is well known that molecular oxygen inhibits free-radical polymerization by scavenging the initiator radicals, which not only reduces the polymerization rate but also affects the mechanical, optical, and structural properties of the cured systems. The mechanism of O_2 inhibition is represented in Figure 2.17. As a result of a photooxidation reaction, peroxy radicals (or hydroperoxides or alcoxy radicals) are generated, which are less reactive toward monomer to initiate radicals

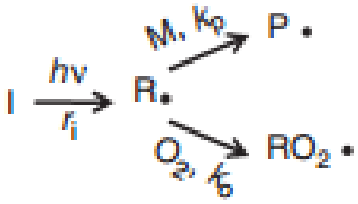


Figure 2.16 : Schematic showing the photoinitiated radical polymerization in the presence of oxygen.

The effect of oxygen can be reduced by increasing the initiator concentration and light intensity,but again, higher initiator concentrations will lead to more significant light attenuation with sample depth [60].

2.5.3.6 Volume shrinkage

Volume shrinkage can be attributed to the formation of covalent bonds during photopolymerization bringing monomers, macromers, or prepolymers in a densely packed formation when compared with the initial liquid (viscous) state. Volume

shrinkage is one of the major concerns in radical photopolymerization. When the photopolymerization is performed in a confined surface (coatings) or volume (sealants,dental restorative materials, and biomaterials), a stress is generated due to shrinkage, which continuously competes with the interfacial adhesion and also cohesive strength of the network. This stress may lead to formation of micro- and macro-gaps at the interface between the material and the surface it was attached to. It can also lead to formation of defects in the material if it is larger than the cohesive strength of any component in the system. Volume shrinkage and the stress associated with it are very important for photopolymerized coatings, The presence of additives has a direct effect on volumetric shrinkage. Stress generally increases with filler loading; however, stress can be reduced if the presence of filler reduces the conversion [61].

2.5.3.7 Additives: fillers and pigments

It is a common practice to incorporate fillers or pigments into polymeric systems to enhance mechanical, optical, electrical, and thermal conductivity properties and stimuli response. When being used in photopolomerizable systems, the nature of these fillers such as size and size distribution, morphology, aspect ratio, surface chemistry and catalytic activity, thermal conductivity, flow properties, and most importantly optical properties, such as light absorption and light scattering, strongly affects the photopolymerization reactions. The fillers can decrease the amount of light that can be absorbed by the photoinitiator by directly absorbing the light (i.e., screening effect). They can also provide a photocatalytic or photosensitizing effect [62, 63].

It is possible to generate radicals without direct excitation by using a photosensitizer that absorbs the incoming light, generates a radical, and transfers the radical to the initiator. There are also compounds that act as photostabilizers to reduce the detrimental effects of prolonged exposure, oxygen, humidity, and toxic compounds, which may lead to decoloration, defects, and loss of adhesion.

2.5.4 Photopolymerization on acrylate system

Acrylic monomers contain unsaturated double bonds (vinyl groups), and consequently cure by addition polymerization involving free radical reaction. Free radical producing compounds such as peroxides, sulfones are added to acrylic resins to initiate polymerization. Free radical polymerization of acrylics may also be induced by

exposure to UV or visible light [64]. In free radical initiated systems of acrylate monomers, the presence of oxygen in the system results in some sort of inhibition or termination, as the peroxide formed prevents propagation of the polymerization reaction. The inflow of oxygen is reduced or eliminated by superimposition of a cover sheet over the photosensitive layer. In some instances, conditioning to exchange the oxygen present in the coating with an inert gas, e.g., nitrogen. In other instances, additives that act as oxygen scavengers are incorporated in the coating layer. However, the oxygen inhibition effect also has a positive aspect in that it prevents premature polymerization during storage [65].

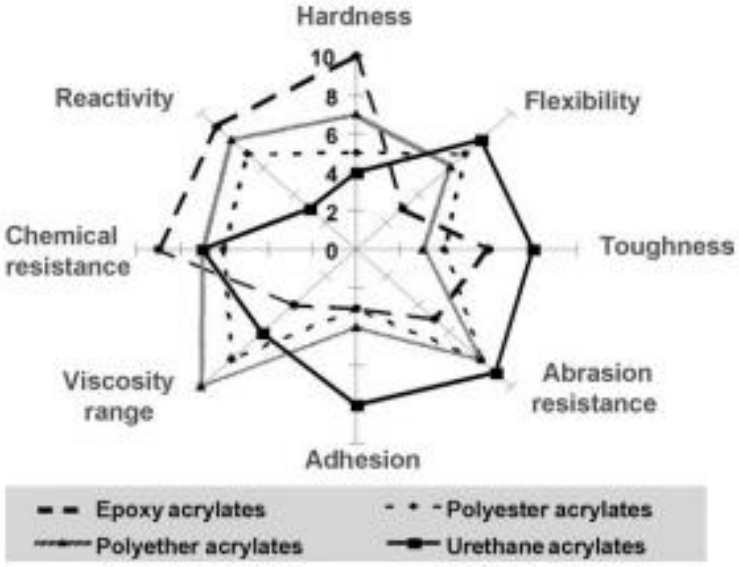


Figure 2.17 : Generalized properties of typical resins of the different UV curable acrylate resin classes.

2.5.5 Radiation curing coatings

Since 1980's there have been many significant changes in surface coatings which have necessitated major changes in the resins used. Radiation curing coatings and inks are formulations of components that contain reactive groups which react with each other after exposure to energy-rich radiation. In general there is no physical drying involved in the curing mechanism.

For curing such high solid con-tent formulations, photopolymerization is an effective approachowing to its advantages such as high curing speed, low energyconsumption, low operation temperature, and less environmental pollution by avoiding volatile organic solvents [66]. In addition,acrylate-based resins and reactive diluents are

preferred in mostphotocuring applications because of their superior reactivity. To start radical photopolymerization, the generation of primaryradicals is necessary. This requires the addition of specific pho-toinitiator compounds that typically decompose into radicals byexposure to light of appropriate wavelengths or abstract a hydro-gen atom from suitable donors (co-initiators) producing initiatingradicals. Because the most common light source in UV curing is themercury arc lamp, the absorption characteristics of photoinitiatorsshould be tuned to its spectrum. Thus, the efficiency of photoini-tiators to convert photons into radicals as well as the quenching ofthose radicals by inhibitors, such as oxygen molecules dissolved inthe acrylate formulation, controls the amount of the photoinitiatorfor obtaining high polymerization rates [67].

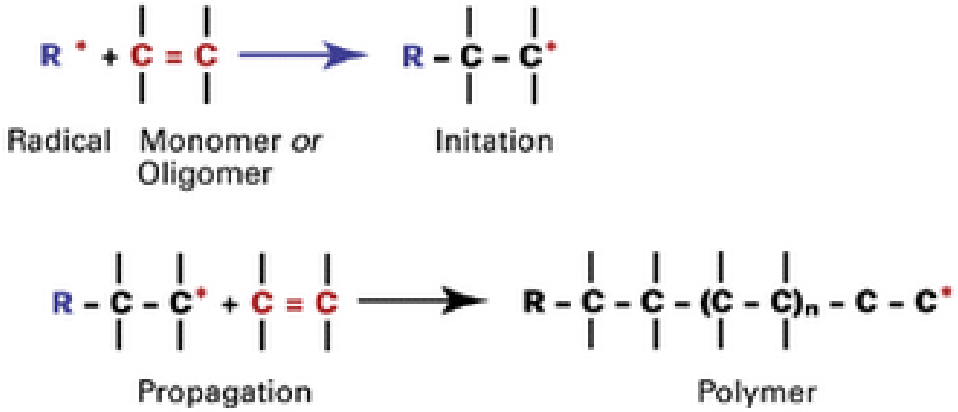


Figure 2.18 : Basic free radical polymerization.

Since 1980's there have been many significant changes in surface coatings which have necessitated major changes in the resins used. There was a time when the surface coatings industry dealt with a relatively small number materials and processes for making paints and varnishes.

The main functions of a coating are thus on the one hand to ensure the desired appearance (colour, gloss) and on the other hand the necessary protection, against corrosion, stone chipping, scratches, abrasion or chemical attack, like red wine, coffee or mustard on furniture coatings or acid rain, tree resins or bird excrements on automotive coatings.

The chemical resistance of the coating surface is usually tested according to occurring or anticipated stresses. Automotive coatings, for example, are subjected to a variety of

chemicals, like acid rain, bird excrements, tree resins, gasoline and so on, which may act upon the surface at various climate conditions, for example, at temperatures as high as 80◦C. These chemicals should not leave any marks or damage at the coating surface [68].

The UV curing process is predominantly determined by the desired application of the coating. The intended end-product governs the substrate to be coated. This may be an abrasion resistant clear coat for ready-to-install parquet or an overprint varnish for paper cards, a coloured base coat and a clear coat for plastic automotive parts or metal coils, as well as a flexible protective coat for window frames. The function of the coating, for instance the colouration of the part, the protection against corrosion, scratching, chemical attack or against weathering deterioration, determines the type and property requirements of the coating as well as the thickness required.

UV curing in general offers a number of advantages over competitive coatings, while some can be related to costs, others relate to performance, environmentally compliance or processes not achievable with other methods. UV curing in its basics is a fast, room temperature curing process indicating low energy consumption and requiring little space for the equipment.

UV curable coatings are mainly used in such industrial applications where thermal curing is hardly possible, like curing of coatings on temperature sensitive substrates, like wood, paper and plastics, and in imaging applications, where only selected areas should be polymerized, like in polymer printing plates and photoresists. Specific applications of photocurable coatings are clear coats for parquet, furniture, vinyl flooring, on plastic substrates (skies, boards), compact discs, headlight lenses, overprint varnishes (posters, high gloss packaging), adhesives, protective coatings for optical fibres, electronic parts. Applications of photocurable coatings on metals (automotive, coil coating) and exterior uses are just emerging. These applications cover a large range of properties.

3. EXPERIMENTAL

3.1 Materials

In synthesis of materials, hyperbranched polyester polyol (Boltorn® H20) (Perstorp), acrylic acid (stabilized with hydroquinone monomethylether) (Merck), toluene-4-sulfonic acid monohydrate (p-toluene sulfonic acid monohydrate) (Merck), toluene (Merck), hydroquinone (Merck), were used. In the preparation of film formulations of materials, Ebecryl® 605 (UCB Chemicals), Desmolux U-500 (Bayer), DPGDA (Sartomer Chemicals), Irgacure 184 (Ciba Chemicals) were used.

Boltorn® H20 was supplied by Perstorp AB, Sweden is an hyperbranched polyester polyol has 16 terminal hydroxyl groups, with a nominal molecular weight of 1750 g/mole. The product is amorphous with a Tg of 25 °C.

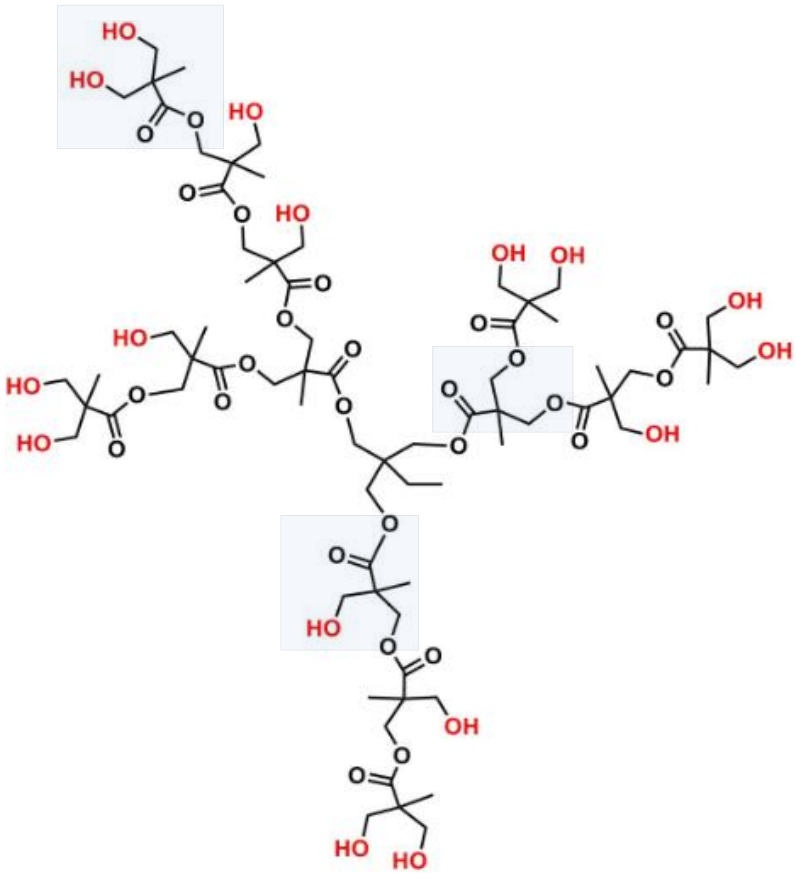


Figure 3.1 : Hyperbranched polyester polyol, Boltorn H20.

Toluene-4-sulfonic acid monohydrate (p-toluene sulfonic acid) is an organic compound with the formula $CH_3C_6H_4SO_3H$. It is a white solid that is soluble in water, alcohols, and other polar organic solvents. Its molecular weight is 190 g/mol.

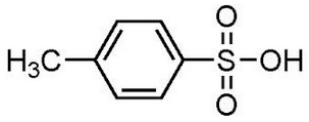


Figure 3.2: Toluene-4-sulfonic acid monohydrate.

Acrylic acid is a clear, colorless liquid with a characteristic acrid odor. It is miscible with water, alcohols and ethers. It is the simplest unsaturated carboxylic acid, consist of a vinyl group connected directly to a carboxylic terminus. Acrylic acid will undergo the typical reactions of a carboxylic acid, as well as reactions of the double bond similar to those of the acrylate esters. It lends itself to polymer preparation as well as use as a chemical intermediate. Acrylate esters, both mono- and multifunctional, are generally prepared from acrylic acid. Acrylic acid is used in the production of coatings, elastomers, adhesives, thickeners, super- absorbents, acrylic esters, and fiber sizing. Its molecular weight is 72.06 g/mol.

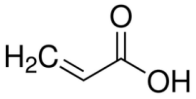


Figure 3.3: Acrylic acid.

Hydroquinone is a white solid aromatic organic compound that is a type of phenol, having the chemical formula $C_6H_4(OH)_2$. Its chemical structure, features two hydroxyl groups bonded to a benzene ring in a paraposition. As a polymerization inhibitor, hydroquinone prevents polymerization of acrylic acid, methyl methacrylate, cyanoacrylate, and other monomers that are susceptible to radical-initiated polymerization. This application exploits the antioxidant properties of hydroquinone. Its density is 1,3g/cm^3 and molecular weight is 110.11 g/mol.

Figure 3.4 : Hydroquinone.

Ebecryl® 605 is commercial epoxy diacrylate used in film formulations as base resin. Films of Ebecryl® 605 cured via ultraviolet light (UV) demonstrate high gloss, surface hardness and superior chemical resistance.

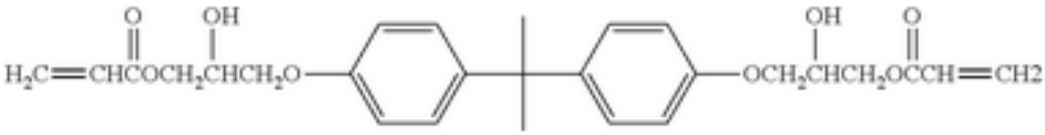


Figure 3.5 : Ebecryl 605.

Dipropyleneglycoldiacrylate (DPGDA) is used as reactive diluent in film formulations to reduce viscosity and component of crosslinking. It is particularly useful in coatings and inks where improved flexibility and adhesion are desired in combination with good moisture resistance. It has also low viscosity, fast curing, low volatility, good dilution . Its molecular weight is 242 g/mol.

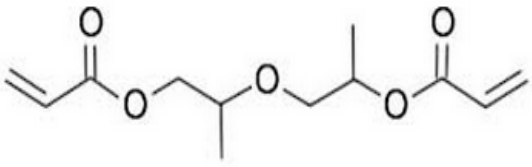


Figure 3.6 : Dipropyleneglycoldiacrylate.

Irgacure 184 from Ciba Specialty Chemicals is a highly efficient non-yellowing photoinitiator which is used to initiate the photopolymerisation of film formulations. Its molecular weight is 204.3 g/mol.

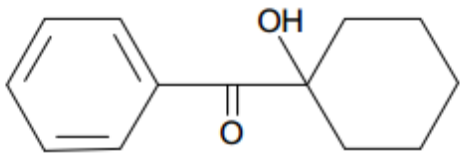


Figure 3.7 : Irgacure 184.

Desmolux® U-500 is unsaturated aromatic urethane acrylate. It is used in the formulation of radiation-curing coatings for the coating of wood, furniture, paper, parquet, cork and films. Coatings formulated with Desmolux® U 500 are characterized

by high flexibility, good coin test behavior and high abrasion resistance, in particular according to the grit feeder method.

3.2 Equipments

3.2.1 Fourier transform ınfrared spectroscopy (FT-IR)

Infrared analyses were performed with Thermo Scientific Nicolet IS 10 FT-IR spectrometer.

3.2.2 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H NMR measurements were recorded in $DMSOd_6$ using a Agilent VNMRS 500 MHz spectrometer.UV curing machine

3.2.3 UV curing machine

UV curing of the films were performed with EMA UV curing system.

3.2.4 Thermogravimetrical analysis (TGA)

Thermogravimetric analyses were performed with Thermal Analysis TGA Q50 instrument at a heating rate of 20 °C/min.

3.2.5 Contact angle measurement

The contact angles of cured films were measured by KSV CAM 100 instrument.

3.2.6 Gloss measurement

The gloss of cured films were measured by BYK-Gardner (Micro-TRI) gloss meter with 20^{o}, 60^{o} and 85^{o}.

3.2.7 Pendulum hardness tester

Pendulum hardness of films were measured with BYK Gardner Konig Pendulum Hardness instrument.

3.2.8 Tensile loading machine

Tensile modulus, tensile strength and elongation at break values of samples were measured with Zwick Z010 Universal Tensile Tester instrument.

3.2.9 Determination of Hydroxyl Number

The hydroxyl number is defined as the quantitative value of the amount of hydroxyl groups. The hydroxyl number(or hydroxyl index) is expressed as miligrams of potassium hydroxide equivalent for one gram of the sample (mg KOH/g). The most important analytical method for hydroxyl number determination is the reaction of the terminal hydroxyl groups with the acidic carboxyl groups. The sample is titrated with aqueous KOH. The acidic carboxyl groups resulting from this reaction are neutralized with the equimolecular quantity of potassium hydroxide. Hydroxyl number is calculated by the value of consumed volume of KOH after titration. **(3.1)**

$$OH = \frac{(V2-V1)*N*56.1}{m} \quad \textbf{(3.1)}$$

Where:

OH= hydroxyl value of the sample (as such) in mg KOH/ g resin

V_1 = ml of potassium hdroxide solution needed for the sample

V_2 = average ml of potassium hydroxide solution needed fort he blank

N= normality of the potassium hydroxide solution

m= weight of the sample in g

AV= Acid value of the sample (as such)

3.3 Synthesis

3.3.1 General procedure of synthesis acrylated hyperbranched-polyester

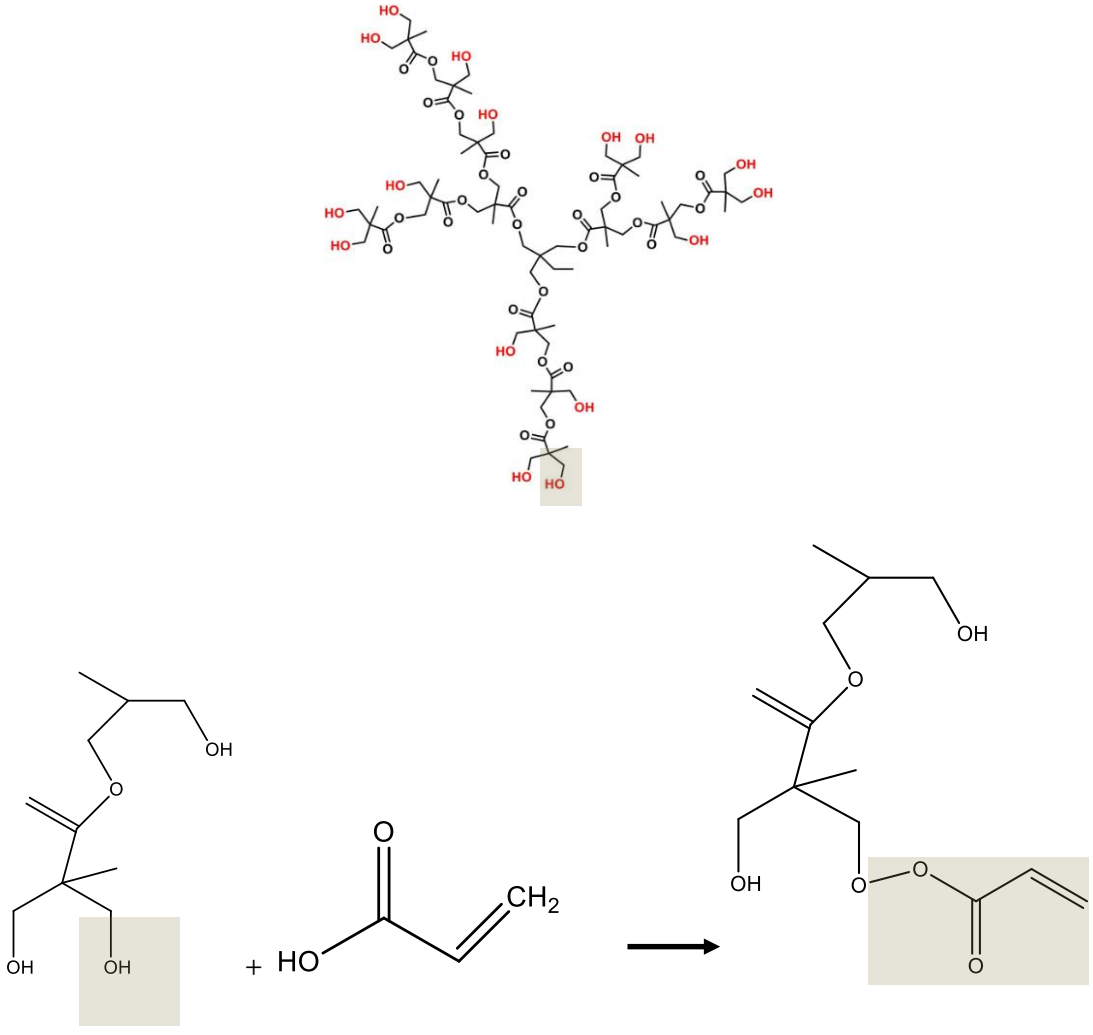
Boltorn® H20 were placed in a three-necked round bottom flask equipped with a thermometer, dropping funnel, dean-stark apparatus, a reflux condenser a magnetic stirrer, a $CaCl_2$ tube, under nitrogen atmosphere at room temperature. It was heated until it melted (ca. 90 min) in an oil bath pre-set to 120 ˚C, in order to break the hydrogen bonds that forms in the material upon standing.

Then acrylic acid was added by one drop in a per second using dropping funnel. On the other hand catalytic amounts of the inhibitor hydroquinone and toluene were added and the temperature were set to 110 ˚C. When a homogenous mixture of the added reagents was obtained, the catalyst, p-toluene sulfonic acid was added. The reaction mixture was refluxed for 3 hours under constant stirring and air flow to prevent premature cross-linking.

After 30 minutes from the beginning of reaction, amount of sample was taken to be analyze in FT-IR spectrometer to control and record the acrylic C=C double bond formation in the structure. We observe the peak of formation acrylic C=C double bond at 1635-1640 cm^{-1} in the IR spectra.

During the reaction, samples were taken from the mixture in order to be checked acid value regularly, after 1 hour from adding p-TSA until the end of the reaction. When acid value is below 10, the reaction was ended and it took 3 hours. The final product was dried via vacum at ambient temperature to remove toluene.

The final degree of acrylation of the synthesized materials was determined by ^{1}H NMR spectroscopy.



(functional OH group Boltorn H20) (acrylic acid) (acrylated functional group of of Boltorn H20)

Figure 3.8 : Synthesis reaction of acrylated hyperbranched polyester, Boltorn H20.

According to rate of mmols of OH groups which belong to H20, and acrylic acid mmol, Boltorn H20 was acrylated partially with 25%, 50%, 75%, 100%. If the rate of OH groups and acrylic acid is 1, acrylation degree was 100%. And also when the moles of acrylic acid was half of mmols of OH groups, acrylation degree was 50%. By using this proportion, amounts of other ingredients were determined for each acrylation-esterification reaction and 25%, 50%, 75%, 100% acrylated hyperbranched polyesters were synthesized. For each acrylation degree, amounts of chemicals are given in Table 3.1.

Table 3.1 : Amount of chemicals are used for each different acrylation degree

	PAB25	PAB50	PQB75	PAB100
Boltorn H20 OH group mmol	44.83mmol	44.83mmol	44.83mmol	44.83mmol
Acrylic acid	11.21mmol	22.415 mmol	33.62mmol	44.83mmol
Hydroquinone(g)	0.025 g	0.025 g	0.025 g	0.025 g
pTSA	0.05 g	0.05 g	0.05 g	0.05 g
Toluene	20 ml	20 ml	20 ml	20 ml

25% acrylated hyperbranched polyester was named PAB25, 50% acrylated hyperbranched polyester was named PAB50, 75% acrylated hyperbranched polyester was named PAB75 and 100% acrylated hyperbranched polyester was named PAB100. The final degree of acrylation of the synthesized materials were calculated from ^{1}H NMR spectroscopy.

3.4 Preparation of Formulations

3.4.1 Preparation of test samples

3.4.1.1. Preparation of free films

UV curable coating formulations were composed of 45 % urethane-acrylate to optimize adhesion and flexibility; 47 % epoxy acrylate to provide hardness with excellent corrosion protection and chemical resistance; 5% dipropyleneglycoldiacrylate as reactive diluent to adjust the viscosity of coating formulations and enable to solubilization of the photoinitiator; 3% Irgacure 184 as photoinitiator. These formulations were modified by replacing epoxy acrylates with partially acrylated Boltorn H20 (PAB) from 5% to 20 %.

Ingredients of the formulations were mixed homogeneously and then were left in vacuum oven for approximately 30 minutes to remove the air in order to avoid bubbles formation in the final films. After the vacuum step, the formulations were poured into the teflon moulds with dimensions of 1 mm x 10 mm x 50 mm. Then the samples were cured by UV processor machine (EMA, 120W/cm, λ max = 365 nm, medium pressure mercury UV lamps) donated with adjustable conveyor speeds.

3.4.1.2. Preparation of coated plexiglass plates

1 g formulations was prepared according to the proper ratios for each film were placed on plexiglass surface and samples were cured in UV processor machine (EMA) passed several times. Coated samples were kept at room temperature for a couple of days before performing tests.

3.4.2. Preparation of formulations

1g film formulations was prepared according to the proper ratios for each film as given in section 3.4.1.1. The formulations were poured in the spaces of the teflon moulds and the samples were cured by UV curing machine for adequate pass numbers. Composition of formulations were given in Table 3.2-5. The films were cured by 15 passes in UV curing machine. Cured films were kept at room temperature for a couple of days before performing the related tests which are tensile test, gel content test, TGA and solvent resistance.

Table 3.2 : Formulations of the films prepared with %100 acrylated hyperbranched Polyester Polyol Boltorn H20 (PAB100).

	Blank	PAB100-5	PAB100-10	PAB100-15	PAB100-20
PAB100 %	0	5	10	15	20
Ebecryl 605 %	47	42	37	32	27
Desmolux U-500%	45	45	45	45	45
DPGDA %	5	5	5	5	5
IRGACURE184 %	3	3	3	3	3

Table 3.3 : Formulations of the films prepared with %75 acrylated hyperbranched polyester polyol Boltorn H20 (PAB75).

	PAB75-5	PAB75-10	PAB75-15	PAB75-20
PAB75 %	5	10	15	20
Ebecryl 605%	42	37	32	27
Desmolux U-500 %	45	45	45	45
DPGDA %	5	5	5	5
IRGACURE184 %	3	3	3	3

Table 3.4 : Formulations of the films prepared with %50 acrylated hyperbranched polyester polyol Boltorn H20 (PAB50).

	PAB50-5	PAB50-10	PAB50-15	PAB50-20
PAB50 %	5	10	15	20
Ebecryl 605 %	42	37	32	27
Desmolux U-500 %	45	45	45	45
DPGDA %	5	5	5	5
IRGACURE184 %	3	3	3	3

Table 3.5 : Formulations of the films prepared with %25 acrylated hyperbranched polyester polyol Boltorn H20 (PAB25).

	PAB25-5	PAB25-10	PAB25-15	PAB25-20
PAB25 %	5	10	15	20
Ebecryl 605 %	42	37	32	27
Desmolux U-500 %	45	45	45	45
DPGDA %	5	5	5	5
IRGACURE184 %	3	3	3	3

3.5 Analysis

Following tests; Infrared Analysis (IR), Thermal Gravimetric Analysis (TGA), Pendulum Hardness, Contact Angle Measurement, Gloss and Tensile tests, Pencil Hardness, Solvent Resistance and Gel Content were applied to investigate

characteristic, thermal, chemical and mechanical properties and behavior of films and coating the samples.

3.5.1 Infrared analysis

FT-IR was used for characterizaton of synthesized products.

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

3.5.2 Thermal gravimetric analysis

TGA was used to determine weight loss temperatures and char yields of cured films. Film samples of 5-15 mg were placed in the sample pan and heated to 800°C under N_2 at an applied heating rate of 20°C /min.

Thermogravimetry has become a general method for comparing the thermal stability of polymers. TGA measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere [69]. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. In comparing thermal stability, it should be remembered that TGA measurements only record the loss of volatile fragments of polymers, caused by decomposition. TGA cannot detect any chemical changes or degradation of properties caused by cross-linking [70].

3.5.3 Gel content measurement

Gel content measurements were made against acetone by Soxhlet extraction for 6 hours. A cured film samples (m_1) were accurately weighted, and extracted with acetone in Soxhlet ectractor for 6 h. The extracted film was dried until a constant weight (m_2). Gel content of the cured film was calculated with this equation:

Gel content (%) = $(m_2/m_1) \times 100\%$

m_1 = initial weight of film

$m_{2=}$ residual weight of the cured film

3.5.4 Solvent resistance

The solvent resistances of the cured films were made against various solvents by immersing the cured film sample (m_1) in 10 ml solvent for one day. After drying the films until a constant weight those were reweighted (m_2) and calculated weight loss.

Solvent resistance of cured film was calculated with this equation:

Weight loss (%) = $(m_1-m_2)/m_1$ x 100

m_1 = initial weight of film

$m_{2=}$ residual weight of the cured film

3.5.5 Contact angle measurement

The contact angle (Krüss Easy Drop DSA 16) instrument was used to investigate wetting behavior of coated samples whether products are hydrophilic or hydrophobic.

The contact angle is an important parameter in surface science. It is a common measure of the hydrophobicity of a solid surface.

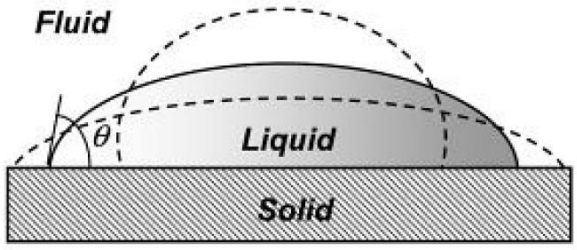


Figure 3.9 : Scheme of a sessile-drop contact angle system.

3.5.6 Gloss test

Gloss instrument was used to determine light reflecting properties of coated samples at 20º, 60º, and 85ºC.

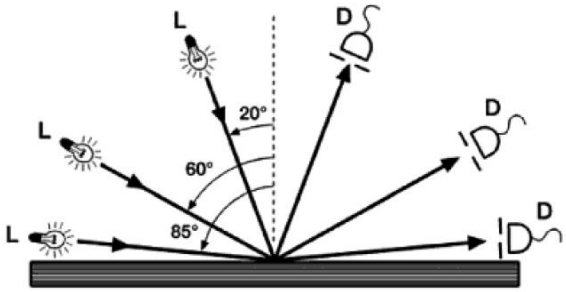


Figure 3.10 : Conventional glossmeter. L, lamp; and D, Detector.

3.5.7 Pendulum hardness tests

Pendulum hardness test was used to investigate wetting behavior of coated samples against applied force. A Koing Pendulum Hardness (BYK-Gardner) tester was used to measure the film hardness.

König pendulum hardness method which is frequently encountered in practice is used for measuring the hardness of the samples. The device itself consists of a pendulum, to the support of which two agate balls are attached. The pendulum is placed on the coating with the two balls 5 mm in diameter and moved 6° away from the position of rest. After releasing the 200 g pendulum the oscillations are recorded by a counter. The measure of damping is the number of oscillations or the time in seconds which elapses until the amplitude of the pendulum has dropped from 6° to 3° [71].

3.5.8 Pencil hardness test

Pencil hardness test was used to determine scratch behavior of coated samples

Pencil hardness is the measure of the hardness of pencil leads (made of different proportions of graphite and clay), commonly ranging from 6B (maximum graphite, hence softest) to 6H (least amount of graphite, hence the hardest) with HB (roughly equal amounts of graphite and clay, hence medium soft/hard) in the middle. Pencil hardness is used in indicating the toughness of surface coatings by testing which number pencil-lead can scratch it.

Figure 3.11 : Pencil hardness and properties.

Pencil Hardness (ASTM D-3363) was performed to check the through cure of coatings. Pencil hardness property of coating was determined using pencil ranging from H to 8H and the pencil that will not scratch the coating reported as pencil scratch hardness.

The pencil hardness results are given in section 4.2.8.

3.5.9 Tensile test

Mechanical properties of the UV-cured films were determined by Zwick Z010 Universal Tensile Tester under a 500 N load cell and using a crosshead speed of 10 mm/min at room temperature. It was used to determine properties such as modulus, elongation at break and strength.

The tensile test serves as the basis for determining several important mechanical properties of materials. In this test, the yield strength, tensile strength, elongation, and reduction in area of a material specimen are determined. In addition, the modulus of elasticity, modulus of resilience, and modulus of toughness of a material are found from the stress–strain curve measured during the tensile test.

The elongation and reduction of area give an indication of the ductility of a material specimen, and the modulus of toughness shows the energy-dissipating capacities of the material, but both ductility and capacity for energy absorption are influenced by such factors as stress concentration, specimen size, temperature, and strain rate. A normally ductile material such as mild steel will behave in a brittle manner under conditions of low temperature, high strain rate, and severe notching. On the other hand, normally brittle materials will behave ductile under high hydrostatic pressures and temperatures. Therefore, assessment of the ductility and energy-absorbing capacity of a material must be made by taking into consideration the service conditions of the final product [72].

4. RESULTS AND DISCUSSION

In this thesis, hydroxyl functional hyperbranched aliphatic polyester, Boltorn® H20, was partially acrylated up to 25%, 50%, 75% and 100% with acrylic acid via esterification reaction. This partially acrylated hyperbranched polyesters were utilized as oligomers in UV curable coatings by gradual replacement of epoxy acrylate oligomer. The effects of partially acrylated Boltorn® H20 against epoxy acrylates in coating formulations were evaluated. The mechanical, thermal and physical properties of the each UV-cured and coated films were investigated.

4.1 Synthesis of Partially Acrylated Hyperbranched Polyester

Hyperbranched polyester Boltorn® H20 was partially acrylated up to 25%, 50%, 75%, 100% with acrylic acid according to the procedure described in section 3.3.1. The ratio of mmols of acrylic acid and OH groups were included in Boltorn® H20, were determined as given table 3.1 depend on desired acrylatin degree.

During the reaction, FT-IR was recorded to follow the acrylic C=C double bond formation in the structure. The peak of C=C double bond was obtained at 1635 cm^{-1} for acrylate groups in FT-IR spectrum was given in figure 4.2.

The reaction was monitored periodically by checking the acid value through the titration method was given in section 3.2.9, and stopped when the acid value was below. Decreasing the acid value show that increasing the acrylated OH groups in Boltorn H20.

The reaction was carried out esterification reaction. Since the reaction type, dean-stark apparatus was used to remove water formed as result of the reaction at high temperature. The reaction mechanizm of acrylation the OH groups is given in Figure 4.1.

On the other hand the temperature controll was the most important parameter in synthesis because of the formation crosslinking. When the temperature is above 110 $^{\circ}C$, the gelation was appear easily.

The final degree of acrylation of the synthesized materials were calculated from ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of Boltorn H20 is given Figure 4.3.

The ^{1}H NMR spectrum of PAB100, is given Figure 4.4, shows the peak between 3.5-3.8 ppm is assigned to the methylene proton attached to the primary alcohol group [-CH_2-OH] and 4.0-4.2 ppm is assigned to the methylene protons attached to the ester unit [-CH_2-OCO-]. The H-bonding of hydroxyl in the molecule does not allow well design signals for resolved signals for –OH groups at 4.6 ppm terminal and 4.9 ppm for linear repeating units.The peaks between 5.85-6.4 ppm are aasigned to double bond protons of acrylic peaks [-CH=CH_2-].

And result of the reaction, Boltorn® H20 was acrylated at four different acrylation percent: 25%, 50%, 75%, 100%.

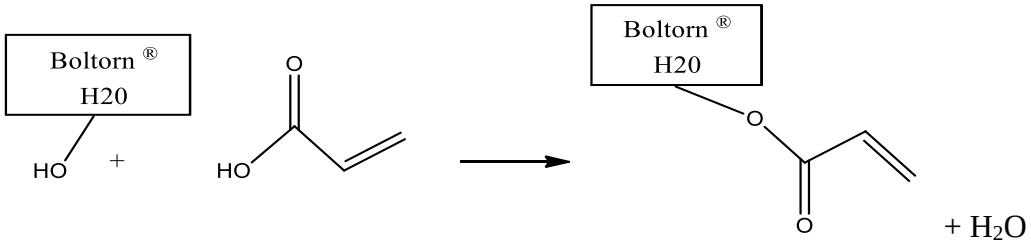


Figure 4.1 : Synthesis reaction of acrylated hyperbranched polyester

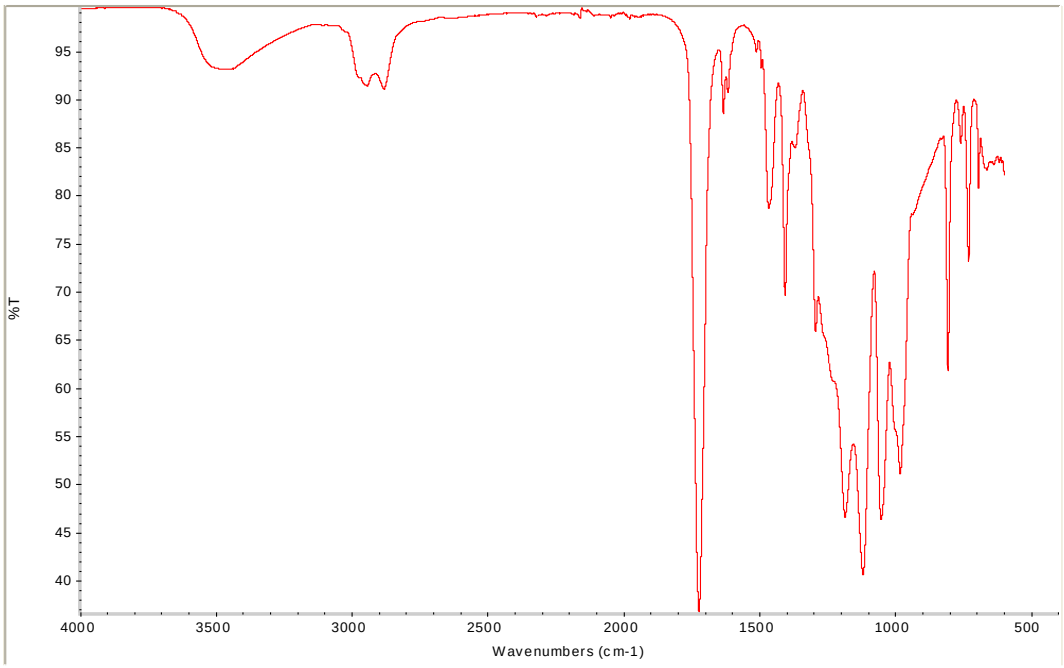


Figure 4.2 : FT-IR spectrum during the synthesis of acrylated hyperbranched polyester.

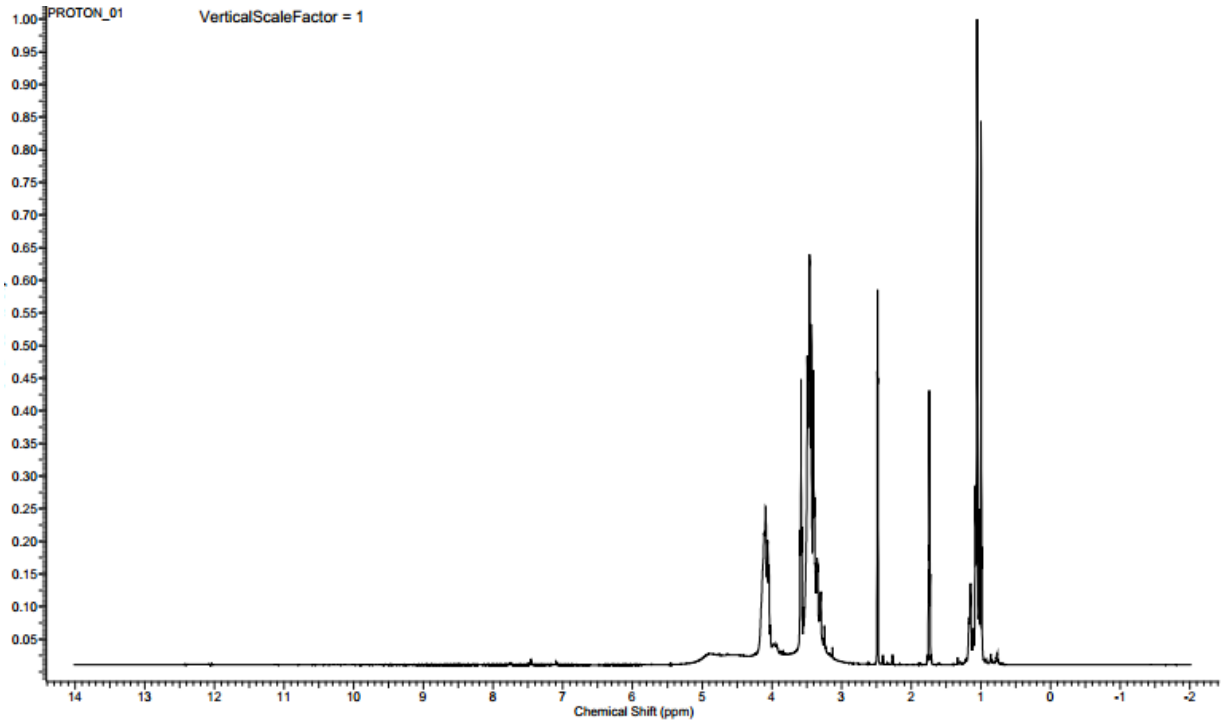


Figure 4.3 : ^{1}H NMR spectrum of hyperbranched polyester polyol, Boltorn H20.

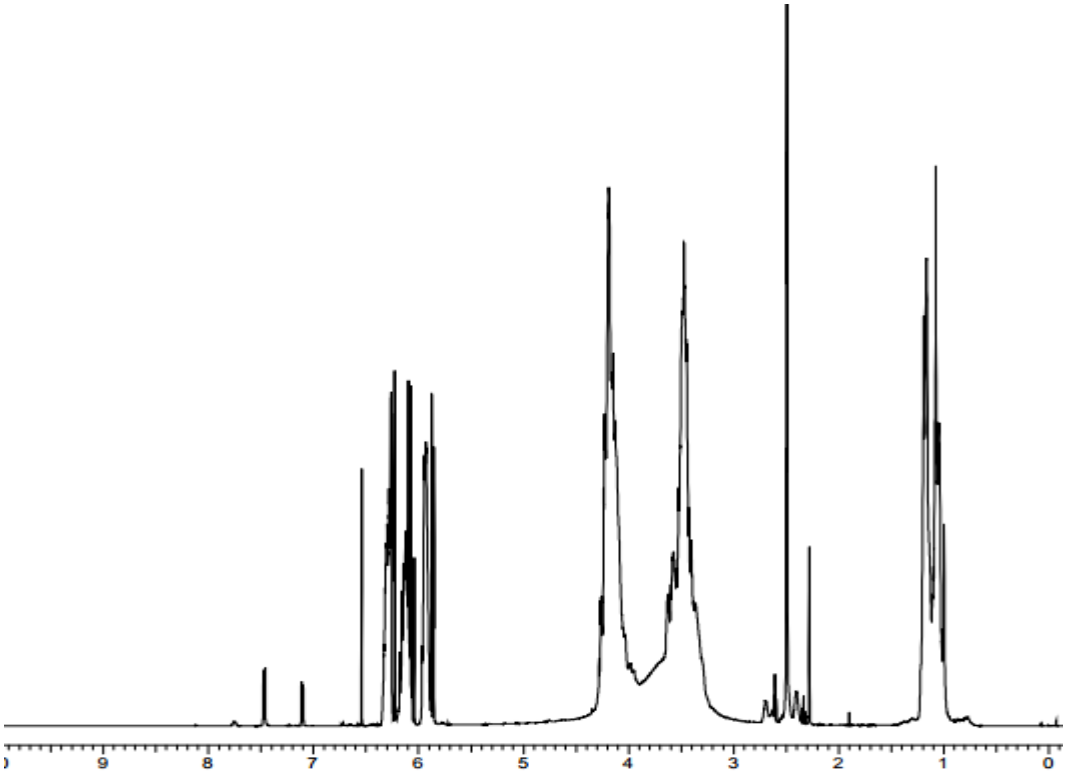


Figure 4.4 : ^{1}H NMR spectrum of acrylated hyperbranched polyester polyol, Boltorn H20.

4.2 Film Formations

UV curable compositions were prepared by mixing aromatic urethane acrylate, aromatic epoxy acrylate, DPGDA, photoinitiator-Irgacure and partially acrylated hyperbranched polyester. All formulations were prepared according to procedure mentioned in section 3.4.2 and have different amount of acrylated hyperbranched polyesters and aromatic epoxy acrylate as given in table 3.2-5.

All the test were performed to the cured and coated films.

Table 4.1 : Definition of the films codes which were prepared by partially acrylated hyperbranched polyester.

PAB100-5 The film was derived from 100% acrylated hyperbranched polyester by adding 5% of its own weight.
PAB100-10 The film was derived from 100% acrylated hyperbranched polyester by adding 10% of its own weight.
PAB100-15 The film was derived from 100% acrylated hyperbranched polyester by adding 15% of its own weight.
PAB100-20 The film was derived from 100% acrylated hyperbranched polyester by adding 20% of its own weight.
PAB75-5 The film was derived from 75% acrylated hyperbranched polyester by adding 5% of its own weight.
PAB75-10 The film was derived from 75% acrylated hyperbranched polyester by adding 10% of its own weight.
PAB75-15 The film was derived from 75% acrylated hyperbranched polyester by adding 15% of its own weight.
PAB75-20 The film was derived from 75% acrylated hyperbranched polyester by adding 20% of its own weight.
PAB50-5 The film was derived from 50% acrylated hyperbranched polyester by adding 5% of its own weight.
PAB50-10 The film was derived from 50% acrylated hyperbranched polyester by adding 10% of its own weight.
PAB50-15 The film was derived from 50% acrylated hyperbranched polyester by adding 15% of its own weight.
PAB50-20 The film was derived from 50% acrylated hyperbranched polyester by adding 20% of its own weight.

PAB25-5 The film was derived from 25% acrylated hyperbranched polyester by adding 5% of its own weight.
PAB25-10 The film was derived from 25% acrylated hyperbranched polyester by adding 10% of its own weight.
PAB25-15 The film was derived from 25% acrylated hyperbranched polyester by adding 15% of its own weight.
PAB25-20 The film was derived from 25% acrylated hyperbranched polyester by adding 20% of its own weight.

4.2.1 Tensile test

Mechanical properties were seriously effected by the crosslink density and chemical structure of the polymeric film. Generally, due to the increased number of functional groups in the hyperbranched polyester the crosslinking density of UV cured films are increased and higher tensile stress values are obtained. The modulus, tensile strength and elongation at break values are used to characterize the mechanical properties of UV films.

The tensile test results for the cured free films prepared with PAB100 are given in Table 4.2.

Table 4.2 : Tensile test results of the films prepared with PAB100.

Sample Code	Modulus (Mpa)	Tensile Strain at Break (%)	Tensile Stress at Break (Mpa)
PAB100-5	555.4	8.1	34.29
PAB100-10	444.6	7.3	21.6
PAB100-15	429.8	8.6	14
PAB100-20	390.5	9.9	8.3

The tensile test results for the cured free films prepared with PAB75 are given in Table 4.3.

Table 4.3 : Tensile test results of the films prepared with PAB75.

Sample Code	Modulus (Mpa)	Tensile Strain at Break (%)	Tensile Stress at Break (Mpa)
PAB75-5	461.8	10.9	12.3
PAB75-10	416.7	11.6	4.9
PAB75-15	417.7	12.0	11.3
PAB75-20	396.92	12.33	15.8

The tensile test results for the cured free films prepared with PAB50 are given in Table 4.4.

Table 4.4 : Tensile test results of the films prepared with PAB50.

Sample Code	Modulus (Mpa)	Tensile Strain at Break (%)	Tensile Stress at Break (Mpa)
PAB50-5	508.4	12.1	3.8
PAB50-10	477.1	12.5	25.8
PAB50-15	310.1	17.04	22.3
PAB50-20	291.2	19.4	17.2

The tensile test results for the cured free films prepared with PAB25 are given in Table 4.5.

Table 4.5 : Tensile test results of the films prepared with PAB25.

Sample Code	Modulus (Mpa)	Tensile Strain at Break (%)	Tensile Stress at Break (Mpa)
PAB25-5	416.4	9.1	19.5
PAB25-10	316.8	8.83	15.0
PAB25-15	230.7	12.1	16.7
PAB25-20	116.3	16.1	11.4

As can be seen from above mentioned Tables, modulus and tensile stress at break values are decreased with increasing amount of partially acrylated hyperbranched polyesters in free films.

Crosslinking density increases with increasing number of functional groups in the hyperbranched polyester. When the acrylation degree is low the number of the OH groups in the system is much higher. As shown in Figure 4.5, modulus values increases with increasing acrylation degree. For each acrylation degree when the amount of partially acrylated hyperbranched polyesters in the film formulation are considered modulus values trends to decrease due to the increasing number of OH groups in the system.

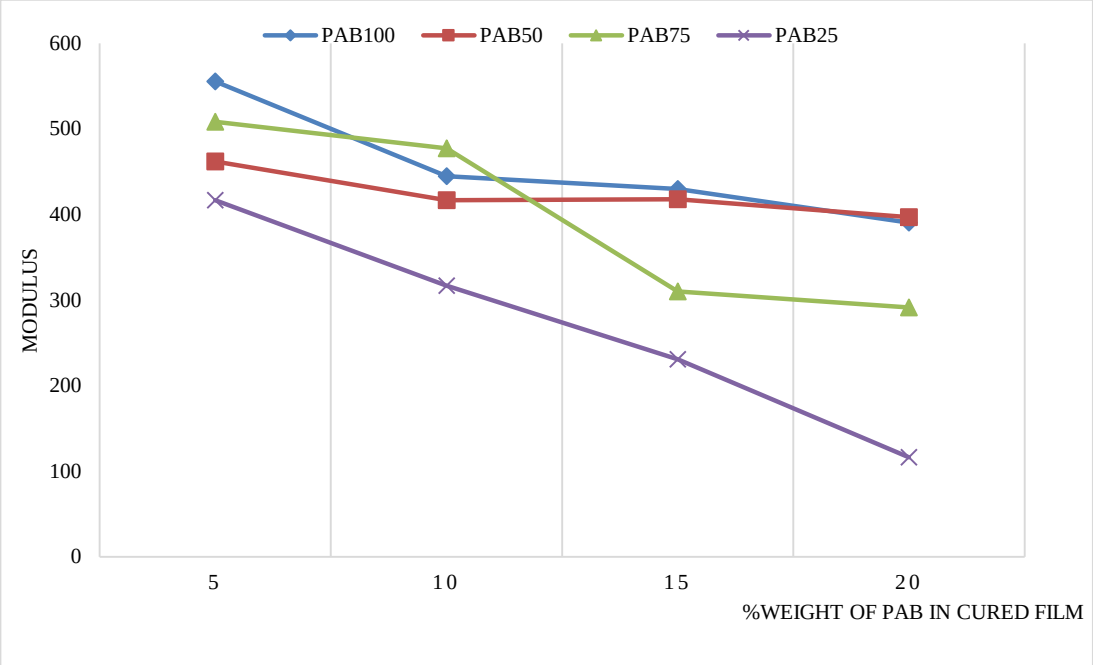


Figure 4.5 : Comparison of the tensile test results of the films with increasing amount of the partially acrylated hyperbranched polyester in free films.

Table 4.6 : Tensile test results of the films prepared with PAB25-PAB50-PAB75-PAB100.

Sample Code	Modulus (Mpa)	Tensile Strain at Break (%)	Tensile Stress at Break (Mpa)
PAB100-15	429.8	8.6	14
PAB75-15	417.7	12.0	11.3
PAB50-15	310.1	17.04	22.3
PAB25-15	230.7	12.1	16.7

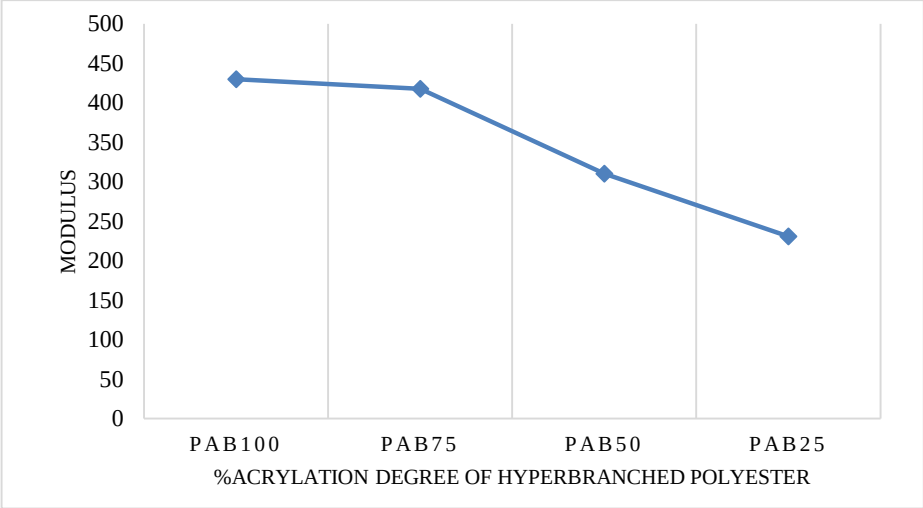


Figure 4.6 : Comparison of the tensile test results of the films with increasing acrylation degree of the the partially acrylated hyperbranched polyester in free films.

The results of the mechanical tests shows that the increase in the acrylation degree improves mechanical properties.

4.2.2 Gel content of cured films

The gel content is important parameter to investigate of the polymerization degree of UV cured films. Gel content test was performed to the cured films via the procedure given in the section 3.5.3 This test was applied to measure the polymerization degree of the cured films. The high gel content values of the film means low weight loss against to solvent and indicate high crosslink formation on the structure.

The results of the gel content tests for the cured free films prepared with PAB100, PAB 75, PAB50, PAB25 are given in Table 4.7.

Table 4.7 : Gel content results of cured films prepared with PAB100, PAB75, PAB50,PAB25.

Sample Code	Gel Content (%weight loss)
PAB100-5	99.24
PAB100-10	95.98
PAB100-15	98.82
PAB100-20	96.10
PAB75-5	98.74
PAB75-10	98.44
PAB75-15	97.98
PAB75-20	98.21
PAB50-5	98.06
PAB50-10	97.04
PAB50-15	100
PAB50-20	99.67
PAB25-5	97.64
PAB25-10	97.90
PAB25-15	95.91
PAB25-20	97.07

Gel content test results of films related to polymerization degree were found over the 96%, its mean that weight loss of films below 3%. The results indicate that crosslinking via acrylated hyperbranched polyester provide high polymerization degree.

On the other hand, neither acrylated degree nor changing amount of acrylated HBPs has effected the degree of crosslinking.

4.2.3 Thermogravimetric analysis

The thermal properties of coatings were performed by using thermogravimetric analysis under nitrogen atmosphere. Heat was increased from 30 ^{o}C to 800 ^{o}C by rate of 20 ^{o}C per a minute.

Table 4.8 : Thermogravimetric results of cured films prepared with PAB100.

Sample Code	50% Loss (^{o}C)	First max. weight loss(^{o}C)	Residue (%)
PAB100-5	435	351	15
PAB100-10	435	350	18
PAB100-15	430	350	10
PAB100-20	428	349	13

Table 4.9 : Thermogravimetric results of cured films prepared with PAB75.

Sample Code	50% Loss (^{o}C)	First max. weight loss(^{o}C)	Residue (%)
PAB75-5	431	349	10
PAB75-10	430	348	9
PAB75-15	427	350	7
PAB75-20	427	348	6

Table 4.10 : Thermogravimetric results of cured films prepared with PAB50.

Sample Code	50% Loss (^{o}C)	First max. weight loss(^{o}C)	Residue (%)
PAB50-5	431	350	6
PAB50-10	431	347	9
PAB50-15	429	349	9
PAB50-20	425	350	9

Table 4.11: Thermogravimetric results of cured films prepared with PAB25.

Sample Code	50% Loss (^{o}C)	First max. weight loss(^{o}C)	Residue (%)
PAB25-5	432	350	9
PAB25-10	430	347	7
PAB25-15	429	351	6
PAB25-20	426	349	8

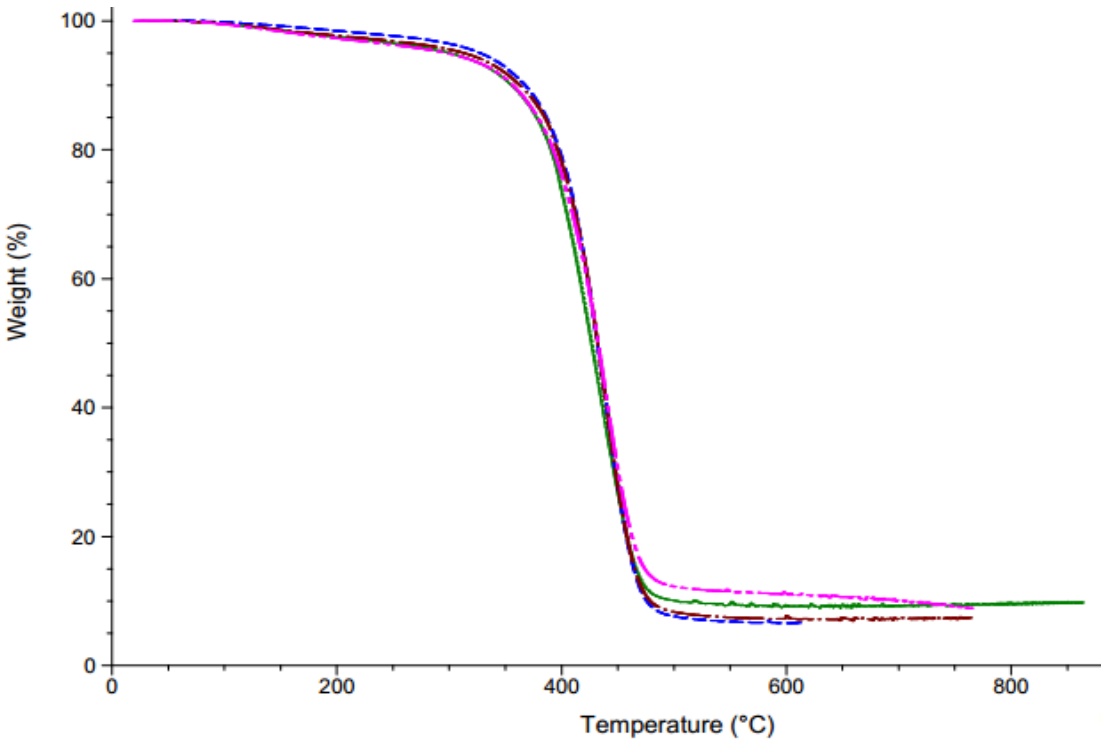


Figure 4.7 : Thermogravimetric graphics of PAB100,PAB75, PAB50, PAB25.

Acrylated hyperbranched polyester based films display similar behavior such as %50 weight loss around 430 ^{o}C and maximum weight loss at around 350 ^{o}C. And char yields values are about 10%.

Increasing acrylation degree and increasing quantity of the acrylated hyperbranched polyester in the free films were not caused different thermogravimetric results.

4.2.4 Solvent Resistance

The chemical resistances of the free films were tested in 10 % solutions hydrochloric acid, sodium hydroxide, acetic acid and chloroform, xylene and methanol solvents.

The films were waited in 10 ml solutions for 24 hours to indicate resistance of cured partially acrylated hyperbranched polyester films.

The solvent resistance test results for the all cured films and the used solvents are given in Table 4.12.

Table 4.12 : Solvent resistance of all films against to all solvents are used.

	%weight loss in Xylene	%weight loss in Methanol	%weight loss in Chloroform	%weight loss in 10% CH_3COOH	%weight loss in 10% HCl	%weight loss in 10% NaOH
PAB100-5	-	< 3	< 3	-	< 3	< 1
PAB100-10	< 1	< 2	< 3	-	-	< 1
PAB100-15	< 1	< 3	< 2	< 2	< 2	< 1
PAB100-20	< 1	< 2	< 5	-	< 3	< 1
PAB75-5	-	< 2	< 5	-	-	< 1
PAB75-10	-	< 3	< 5	< 1	< 2	< 1
PAB75-15	-	< 2	< 4	-	< 1	< 1
PAB75-20	-	< 2	< 2	-	< 2	< 1
PAB50-5	-	< 2	< 5	< 2	< 3	< 1
PAB50-10	< 1	< 2	< 4	< 2	< 3	< 1
PAB50-15	-	<1	< 5	< 3	< 3	< 1
PAB50-20	< 1	< 2	< 5	< 2	< 3	< 1
PAB25-5	< 1	<3	< 5	-	< 2	< 1
PAB25-10	-	< 3	< 2	< 1	< 1	< 1
PAB25-15	-	< 3	< 6	< 2	< 3	< 1
PAB25-20	<1	< 3	< 5	< 3	< 1	< 1

Solvent resistance results show that the films don't have resistance against to chloroform but have resistance to other chemicals and maximum resistance was recorded against to xylene.

The films were placed over the liquid after 24 hours. The acrylated HBPs modified films were broken and gave higher weight loss values after waiting in chloroform.

On the other hand, the results show that acrylation degree and amount of acrylated HBPs in the formulations are no effected on the solvent resistance properties of the films.

4.2.5 Contact angle

Contact angle values are indicated by dropping water on the film surface. Three measurements were recorded and each measurements were taken by one drop water.

Contact angle values are related to hydrophilic or hydrophobic effect of the surface. Average of the values are given as the test result in Table 4.13-17.

Higher contact angle values and more hydrophobic surfaces were obtained by increasing the amount of acrylated PAB.

The contact angle results for the cured films of PAB100 and the used solvents are given in Table 4.13.

Table 4.13 : Contact angle of the films prepared with PAB100.

Sample Code	Water Contact Angle (°)
Blank (for plexiglass)	70.29
PAB100-5	63.09
PAB100-10	65.14
PAB100-15	66.65
PAB100-20	67.92

The contact angle results for the cured films of PAB10075 and the used solvents are given in Table 4.14.

Table 4.14 : Contact angle of the films prepared with PAB75.

Sample Code	Water Contact Angle (°)
Blank (for plexiglass)	70.29
PAB75-5	68.50
PAB75-10	68.14
PAB75-15	68.58
PAB75-20	70.01

The contact angle results for the cured films of PAB50 and the used solvents are given in Table 4.15.

Table 4.15 : Contact angle of the films prepared with PAB50.

Sample Code	Water Contact Angle (°)
Blank (for plexiglass)	70.29
PAB50-5	63.98
PAB50-10	65.31
PAB50-15	67.71
PAB50-20	67.89

The contact angle results for the cured films of PAB25 and the used solvents are given in Table 4.16.

Table 4.16 : Contact angle of the films prepared with PAB25.

Sample Code	Water Contact Angle (°)
Blank (for plexiglass)	70.29
PAB25-5	61.42
PAB25-10	59.33
PAB25-15	59.83
PAB25-20	60.61

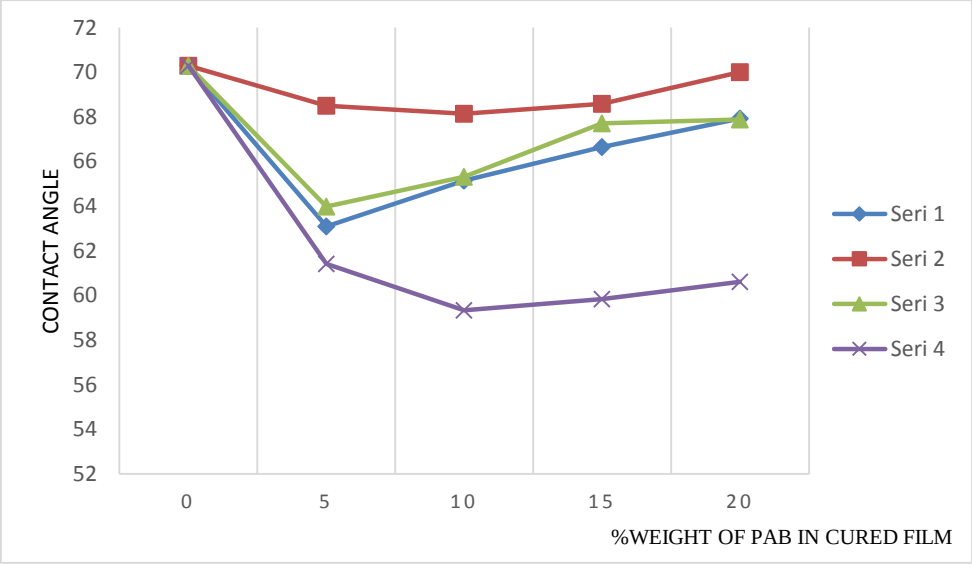


Figure 4.8 : Contact angle test results of the films prepared with PAB25-PAB50-PAB75-PAB100.

Increasing the acrylation degree and amount of the acrylated hyperbranched polyester in cured films causes a decrease in the contact angle values providing more hyrophobic surfaces.

4.2.6 Gloss test

Gloss test applied to the coated plates were measured at the angles of 20º, 60º and 85º. The gloss values were decreased by addition of acrylated PAB.

The gloss test results for the cured films of PAB are given in Table 4. 17-20.

Table 4.17 : Gloss test of the films prepared with PAB100.

Sample Code	Gloss		
	20°	60°	85°
PAB100-5	155	153	104
PAB100-10	154	154	105
PAB100-15	145	148	105
PAB100-20	142	147	102

Table 4.18 : Gloss test of the films prepared with PAB75.

Sample Code	Gloss		
	20°	60°	85°
PAB75-5	157	154	110
PAB75-10	154	147	104
PAB75-15	134	151	102
PAB75-20	145	150	103

Table 4.19 : Gloss test of the films prepared with PAB50.

Sample Code	Gloss		
	20°	60°	85°
PAB50-5	147	151	108
PAB50-10	146	140	107
PAB50-15	138	142	103
PAB50-20	135	137	105

Table 4.20 : Gloss test of the films prepared with PAB25.

Sample Code	Gloss		
	20°	60°	85°
PAB25-5	124	135	97
PAB25-10	115	131	96.3
PAB25-15	118	127	85.14
PAB25-20	109	122	93.9

4.2.7 Pendulum hardness

The hardness of the coating is related to chain flexibility of the molecules and crosslinking density and also it is the main important factor effecting the abrasion and scratch resistance. The pendulum hardness test measures the surface hardness in combination with surface friction.

The pendulum hardness test results for the coated plates are given in table 4.21-24. As a summary of the all results given for pendulum hardness, the increasing the amount of the partially acrylated HBPs decreases the hardness value.

Table 4.21 : Pendulum hardness of the films prepared with PAB100.

Sample Code	Pendulum Hardness (oscillations according to König)
Blank (for plexiglass)	77
PAB100-5	83
PAB100-10	80
PAB100-15	80
PAB100-20	70

Table 4.22 : Pendulum hardness of the films prepared with PAB75.

Sample Code	Pendulum Hardness (oscillations according to König)
Blank (for plexiglass)	77
PAB75-5	84
PAB75-10	79
PAB75-15	79
PAB75-20	68

Table 4.23 : Pendulum hardness of the films prepared with PAB50.

Sample Code	Pendulum Hardness (oscillations according to König)
Blank (for plexiglass)	77
PAB50-5	82
PAB50-10	78
PAB50-15	79
PAB50-20	65

Table 4.24 : Pendulum hardness of the films prepared with PAB25.

Sample Code	Pendulum Hardness (oscillations according to König)
Blank (for plexiglass)	77
PAB25-5	79
PAB25-10	76
PAB25-15	63
PAB25-20	61

4.2.8 Pencil hardness

Pencil hardness test measures the surface hardness in combination with surface scratch. This test provide investigating of surface hardness in addition to pendulum hardness method and it is applied as given in section 3.5.8.

100%acrylated hyperbranched polyester based film formulation gave pencil hardness value of 6H and 25% acrylated hyperbranched polyester based film formulation gave pencil hardness value of 3H. Increasing the acrylation degree make pencil hardness values improved.

Table 4.25 : Pencil hardness of the films prepared with PAB100.

Sample Code	Pencil Hardness
PAB100-5	6H
PAB100-10	5H
PAB100-15	5H
PAB100-20	5H

Table 4.26 : Pencil hardness of the films prepared with PAB75.

Sample Code	Pencil Hardness
PAB75-5	5H
PAB75-10	5H
PAB75-15	5H
PAB75-20	>5H

Table 4.27 : Pencil hardness of the films prepared with PAB50.

Sample Code	Pencil Hardness
PAB50-5	3H
PAB50-10	3H
PAB50-15	3H
PAB50-20	4H

Table 4.28 : Pencil hardness of the films prepared with PAB25.

Sample Code	Pencil Hardness
PAB25-5	3H
PAB25-10	3H
PAB25-15	3H
PAB25-20	3H

5. CONCLUSION

In this thesis, hyperbranched polyester acrylate has been synthesized and employed as an oligomer in UV-curable formulations. For this purpose hyperbranched polyester Boltorn® H20 was acrylated up to 25%, 50%, 75% and 100% with acrylic acid via esterification reaction according to the described procedure. The formation of the acrylic bonds were followed by FT-IR spectroscopic technique. The peak of C=C double bond was observed at 1635 cm^{-1} for acrylate groups in FT-IR spectrum at the begining of the reaction.

The yields of esterification reactions were determined via ^{1}H NMR spectroscopy, and it was observed that actual degree of acrylations was lower than the targeted degree of acrylations. Increasing the amount of partially acrylated Boltorn (PAB) oligomers in UV curable formulations did not have sıgnificant effect on the mechanical properties of the UV cured fılms due to the presence of non-acrylated OH functional groups which lowers the crosslinking density and provides flexibility to the structure.

Thermal gravimetric analysis, gel content measurement, solvent resistance, contact angle measurement, gloss test, pendulum hardness tests, pencil hardness test applied to the UV-cured films.

The thermal stability of the UV-cured films were investigated by thermogravimetric analysis technique and all films which were prepared with PAB display similar behaviour such as maximum weight loss at around 350 ^{o}C. And the addition of PAB gave slightly lower thermal stability. The char yield values were low for all films which are in good agreement with the literature.

The contact angle values were measured against to water and increasing amount of the PAB in the UV curable formulations resulted with higher contact angle values and more hyrdophobic surface.Gel content values indicate that partially acrylated Boltorns were succesfully incorporated into UV-curable film formulations. The results show that crosslinking via acrylated hyperbranched polyester oligomers provide high polymerization degree. Coating properties like contact angle and pencil hardness were improved by increasing the acrylation degree and the amount of PAB in UV-curable formulations.

In conclusion, the effects of the partially acrylated hyperbranched resins in UV-curable formulations were investigated and it was observed that acrylation degree has a significant effect on the mechanical properties of the UV-cured films.

6. REFERENCES

[1] **Tomalia. D.A., Christensen J.B., Boas, U.,** 2012, Dendrimers, Dendrons, and Dendritic Polymers. p. 1.

[2] **Voit, B.I.,** 2003, Hyperbranched Polymers: a Chance and a Challenge

[3] **Voit, B.,** 2005, Hyperbranched Polymers, Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 43, pp.2679–2699.

[4] **Bhatnagar, M.S.,** 1996, Concise Polymeric Materials Encyclopedia, Epoxy Resins (Overview), p.p.1,9.

[5] **Chattopadhyay, D.K., Panda, S.S.,** 2005, Progress in Organic Coatings, Volume 54, Issue 1, pp.10-19.

[6] **Decker C.,** 1996, Prog. Polym., 21, pp.593–650.

[7] **Schalley, C.A., Vögtle, F.,** Dendrimers V Functional and Hyperbranched Building Blocks Photophysical Properties Application in Materials and Life Science, p.66.

[8] **Vögtle, F**., **Richardt, G., Werner, N.,** Dendrimer Chemistry Concepts, Syntheses, Properties, Applications, p.15.

[9] **Gauthier, M., Möller, M.,** 1991, Macromolecules.

[10] **Fogelström, L., Antoni, P., Malmstr¨om, E., Hult, A.,** 2006, UV-curable hyperbranched nanocomposite coatings, Progress in Organic Coatings, 55, pp.284–290.

[11] **Hult A, Johansson M, Malmström E, Sörensen,** 1993, Branched Polymer II

[12] **Tomalia D.A., Christensen J.B., Boas, U.,** 2012, Dendrimers, Dendrons, and Dendritic Polymers, p.14.

[13] **Voit B.J.,** 2000, Polym. Sci. Part. A: Polym. Chem., 38, p.2505

[14] **Vögtle, F**., **Richardt, G., Werner, N.,** Dendrimer Chemistry Concepts, Syntheses, Properties, Applications, p:15

[15] **Chimie, C.R.,** 2003, Dendritic polymers Hyperbranched polymers: a chance and a challenge p.p.821,832.

[16] **Şabani, S.,** 2011, Doctora thesis, Istanbul Techniqual University.

[17] **Hult, A., Johansson, M., and Malmström** 1999, Branched Polymer II, Adv. Polym. Sci., Volume 143, p.3

[18] **Fréchet J. M. J.,** 1994 Science 263, p.1710

[19] **Vögtle, F**., **Richardt, G., Werner, N.,** 2009, Dendrimer Chemistry Concepts, Syntheses, Properties, Applications,, p.38.

[20] **Stockmayer, W.H.,** 1943, J. Chem. Phys. 11, pp.45–55.

[21] **Vögtle, F**., **Richardt, G., Werner, N.,** 2009, Dendrimer Chemistry Concepts, Syntheses, Properties, Applications, p.38,39.

[22] **Schalley, C.A., Vögtle, F.,** Dendrimers V Functional and Hyperbranched Building Blocks Photophysical Properties Application in Materials and Life Science, p.10

[23] **Voit, B.I., Lederer, A.,** 2009, Chem Rev., 109, p.5924.

[24] **Wooley, K.L. Hawker, J.M., Pochan, J.M. and Frechet, J.M.J.,** 1993 Macromolecules, 26, p.1514.

[25] **Voit, B.** 2005, J. Polym. Sci. A: Polym. Chem., 43, p.2679.

[26] **Kim, Y.H., Webster, O.W.,** 1992, Macromolecules 25, p.5561.

[27] **Hult, A., Johansson, M., and Malmström, E.,** 1999, Adv. Polym. Sci., 143, p.1.

[28] **Rogunova, M., Lynch, T.Y.S., Pretzer, W., Kulzick, M., Hiltner, A., and Baer, E.,** 2000, J. Appl. Polym. Sci. 77, p.1207.

[29] **Dekker, M.,** 1988, Epoxy resins.

[30] **Pearson, R.A., Yee, A.F.,** 1983, The effect of cross-link density on the toughening mechanism of elastomer-modified epoxies, Polym Mater Sci Eng Prepr Am Chem Soc, 186, p.316.

[31] **Kinloch, A.J.,** 1989, Relationships between the microstructure and fracture behavior of rubber-toughened thermosetting polymers, Adv Chem Ser., 222, p.67.

[32**] Luciani, A., Manson, J.A.E,** 1993, Physical and rheological properties of aliphatic hyperbranched polymers, J. Polym Sci Part B.

[33] **Srivastava, S. K., Singh, I. B.,** 2012, Hybrid epoxy nanocomposites: lightweight materials for structural applications. Polym J, 44, p.334–9.

[34] **Kunz, S.C., Beaumont PWR,** 1981, Low-temperature behavior of epoxy- rubber particulate composites, J Mater Sci, 16, p.52.

[35] **Ozturk A, Kaynak C, Tincer T.,** 2001, Effects of liquid rubber modification on the behavior of epoxy resin, Eur Polym J, 37:2353, p.63.

[36] **Abad, M.J., Barral, L., Cano, J., Lopez, J., Nogueira, P., Ramirez, C.**, **et al,** 2001, Thermal decomposition behavior and the mechanical properties of an epoxy/cycloaliphatic amine resin with ABS, Eur Polym J, 37:1613, p.23.

[37] **Huang, P., Zheng, S., Huang, J., Guo, Q.,** 1997, Miscibility and mechanical properties of epoxy resin/polysulfone blends, Polymer, 38:5565, p.71.

[38] **Hsieh, T.H., Kinloch, A.J., Masania, K., Lee, S.J., Taylor, A.C., Sprenger, S.,** 2010, The toughness of epoxy polymers and fibre composites modified with rubber micro particles and silica nanoparticles, J Mater Sci, 45:1193, p.210.

[39] **Boogh, L., Pettersson, B., Manson, J.A.E.,** 1990, Dendritic hyperbranched polymers as toughеners for epoxy resins, Polymer, 40:2249 p.61.

[40] **Habrard A, Park Y, Halley PJ, Simon G.P.,** 2006, Phase separation, porous structure, and cure kinetics in aliphatic epoxy resin containing hyperbranched polyester., J Polym Sci Part B: Polym Phys;44:889 p.99.

[41] **Ratna, D., Varley, R., Raman, R.K.S., Simon, G.P.,** 2003, Studies on blends of epoxy-functionalized hyperbranched polymer and epoxy resin, J Mater Sci. 38:147, p.54.

[42] **Lim, J.K., Kim, D.K., Hwang, J.Y., Korean, J,** 2003, Ind Eng Chem 14(6), p.818.

[43] **Kim, J.W., Suh, K.D.,** 1998, Colloid Polym Sci, p.p.276,342.

[44] **Young-Jun Parka, Y.J., Lima, D.H., Kima, H.J., Parka D.S., Sun, U.K.,** 2009,UV- and thermal-curing behaviors of dual-curable adhesives based on epoxy acrylate oligomers, International Journal of Adhesion & Adhesives, 29, p.p.710–717.

[45] **Kaczmarek, H., Decker, C.J.,** 1994, Appl Polym Sci, 54, p.2147.

[46] **Auchter, G., Aydin, O., Zettl, A., Satas, D.,** 1999, Handbook of pressure sensitive adhesive technology. Warwick. Satas & Associates;.

[47] **Deligny, P., Tuck, N.,** Resıns for surface coatings VolumeII Alkyds&Polyesters, p.119.

[48] **Wicks, Z.W., Jones, W.N., Pappas, S.P., Wicks, D.A.,** Organic Coatings Science and Technology, Third Edition, p.p.199,200

[49] **Hardeman, G., Misev, T.A., Heyenk, A.,** 1993 WO 93/18,079.

[50] **Hult A, Johansson M, Malmström E, Sörensen** K (1993) WO 93/17,060

[51] **Brenner, A.R., Voit, B.I., Massa, D.J., Turner, S.R.** 1996 Macromol. Symp. 102, p. 47.

[52] **Allen, N.S.,** 2007, Polymer Photochemistry, 36, p.232.

[53] **Guvendiren, M., Purcell, B., Burdick, J.A.,** 2012, Photopolymerizable Systems Polymer Science: A Comprehensive Reference, Volume 9, p.413.

[54] **Crivello, J. V.,** 2012, Photopolymerizable Systems Photopolymerization Polymer Science: A Comprehensive Reference, Volume 4, p.924

[55] **Maag, K., Lenhard, W., Löffles, H.,** 2000, New UV curing systems for automotive applications, Progress in Organic Coatings 40, pp.93-97.

[56] **Studer, K., Decker, C., Beck, E., Schwalm, R.,** 2003, Overcoming oxygen inhibition in UV-curing of acrylate coatings by carbon dioxide inerting: Part II, Progress in Organic Coatings 48, pp.92-101.

[57] **Fouassier, J. P., Ruhlmann, D., Graff, B., Wieder, F.,** 1995, Prog. Org. Coat., 25, p.169.

[58] **Guvendiren, M., Purcell, B., Burdick, J.A.,** 2012, Photopolymerizable Systems Polymer Science: A Comprehensive Reference, 9, pp.422,423.

[59] **Moussa, K., Decker, C. J.,** 1993, Polym. Sci. Part A: Polym. Chem., 31, p.2197.

[60] **O'Brien, A.K., Bowman, C. N.,** 2006, Macromol. Theor. Simul. 15, p.176.

[61] **Guvendiren, M., Purcell, B., Burdick, J.A.,** 2012, Photopolymerizable Systems Polymer Science: A Comprehensive Reference, 9, p.425.

[62] **Rosche, K., Decker, C., Israel, G., Fouassier, J. P.,** 1997, Eur. Polym. J., 33, p.849.

[63] **Timpe, H. J., Kustermann, E., Bottcher, H.,** 1991, Eur. Polym. J., 27, p.429.

[64] **Licari, J.J., and Linda, Y.,** 2005, Adhesives Technology for Electronic Applications p.123.

[65] **Dessaue, R.,** 2006, Habisas PhotopolymerizationInitiators Photochemistry, History and Commercial Applications of Hexaarylbiimidazoles, p.131.

[66] **Mehnert, R., Pincus, A., Janovsky, I.,** 1998, UV & EB Curing Technology and Equipment,Wiley-SITA.

[67] **Bauera, F., Deckerb, U., Naumovb, S., Riedel, C.,** 2014, Photoinitiator-free UV curing and matting of acrylate-basednanocomposite coatings: Part 3, Progress in Organic Coatings 77, p.p.1085–1094.

[68] **Schwalm, R.,** 2007, UV Coatings Basics, Recent Developments and New Applications, Elsevier, p.91.

[69] **Chatloff, R.P., Sircar, A.K.,** 2005, Thermal Analysis of Polymers, Encyclopedia of Polymer Sceince and Technology, John Wiley&Sons.

[70] **Madorsky, S.L.,** 1964, Thermal Decomposition of Organic Polymers, Wiley-Interscience

[71] **Goldschmidt, A., Streitberger, H.J.,** 2003, BASF Handbook on Basics of Coating Technology, BASF Coatings AG, p.22.

[72] **Pilkey, W.,** 2005, Formulas for Stress, Strain, and Structural Matrices 2nd ed, p.57.

CURRICULUM VITAE

Name Surname: Saadet Şeyma ÖZDEMİR

Place and Date of Birth: Mersin**,** 01.11.1987

E-Mail: sseymaozdemir@hotmail.com

B.Sc.: Hacettepe University